Theoretical Research Investigation of High Energy Species

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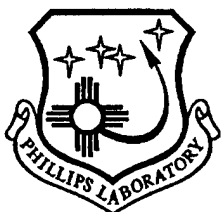
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FOREWORD

This report presents the results of a study performed by United Technologies Research Center, East Hartford CT 06108, under Contract No. F04611-90-C-0009, for Operating Location AC, Phillips Laboratory (RKS), Edwards AFB CA 93524-7048. The program is entitled "Theoretical Research Investigation of High Energy Chemical Species." The Project Manager for Phillips Laboratory was Dr. E. J. Wucherer.
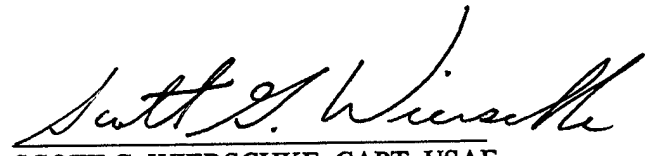
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Helpful guidance during the course of this research program was provided by Captain Peter Dolan, Captain Timothy McKelvey, Dr. Patrick Carrick, and Dr. E. J. Wucherer, who served in succession as Project Managers for this contract.

This report has been reviewed and is approved for release and distribution in accordance with the distribution statement on the cover and on the SF Form 298.

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13. ABSTRACT (MAXIMUM 200 WORDS)

A theoretical investigation was conducted of high energy chemical species that are attractive candidates for advanced propulsion systems. The objectives of this research program were to identify those light element molecular species that have sufficient internal energy to be useful in advanced chemical propulsion systems; to characterize their molecular structure, energy content and structural or radiative stability; to examine the probable kinetic routes for decomposition of these species; to characterize the vibrational and electronic spectra and other static molecular properties; and to propose possible synthesis routes for their formation and subsequent storage. Experimental data collected at other laboratory sites where there were parallel studies of high energy chemical species – specifically, SRI International, Rockwell Science Center, Rocketdyne, and Phillips Laboratory – were iteratively examined and integrated with the results generated by this theoretical investigation.

A goal of this theoretical investigation was to furnish fundamental data and to provide a better understanding of the possibilities of forming chemical compounds that represent advanced high energy sources. It was also intended that this theoretical research effort be carried out with sufficient flexibility to aid in the analysis and guidance of any concurrent experimental programs of synthesis of high energy molecular species. To this end, the tasks of this research program to date have included the following studies: 1) high symmetry and hypervalent structures as advanced oxidizers; 2) azide-like species such as N_7 and NO_2N_3; 3) nitrated cyclic and polycyclic compounds, as further developments of cyclic nitramines such as the HMX and PCN family of propellants; 4) an extensive analysis of dinitramide compounds as potential chlorine-free oxidizers; 5) nitrated ring structures including nitrozoles and azididines; and 6) substituted prismanes.

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high symmetry structures; hypervalent structures; advanced oxidizers; azide-like species; nitrated cyclic compounds; nitrated polycyclic compounds; cyclic nitramines; propellants; dinitramide compounds; chlorine-free oxidizers; nitrated ring structures; nitrozoles, azididines; substituted prismanes

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GLOSSARY

ADN - ammonium dinitramide or $NH_4N(NO_2)_2$ or $H_4N_4O_4$

ADN/GAP - ammonium dinitramide/glycidyl azide polymer

ADNT - 1-amino-3,5-dinitrol-1,2,4-triazole or $C_2H_2N_6O_4$

a-N_2O_2 - asymmetric dinitrogen dioxide

ANT - 1-amino-3-nitro-1,2,4-triazol or $C_2H_3N_5O_2$

AP - ammonium perchlorate

B_2H_6 - diborane

$B(NO_2)_2^-$ - dinitroboride anion

C_2 - group symmetry structure

C_{2v} - group symmetry structure

C_3 - group symmetry structure

C_s - group symmetry structure

$CH_2N_6O_2$ - 1-amino-3-nitrotetrazole

CH_3NO_2 - nitromethane

$C_2H_4N_4O_4$ - 1,3-dinitro-1,3-diazacyclobutane or HEDMX

C_2HNO_2 - nitroacetylene

$C_2N_2O_4$ - dinitroacetylene

CN_2O_2 - nitrylcyanide

$C_2H_2N_4O_3$ - 3-nitro-1,2,4-triazol-5-one or NTO

$C_2H_3N_5O_2$ - 1-amino-3-nitro-1,2,4-triazol

$C_2H_2N_6O_4$ - 1-amino-3,5-dinitro-1,2,4-triazole

$C_2H_2N_6O_4$ - 5-amino-2,4-dinitro-1,3,5,-triaza-bicyclo[2,1,0]pent-2-ene

$C_2HFN_4O_2$ - 1-fluoro-3-nitro-1,2,4-triazole

$C_3H_3NO_2$ - 1-nitropropylene

$C_3H_4N_4O_6$ - 1,3,3-trinitroazididine or TNAZ

$C_3H_6N_6O_6$ - 1,3,5-trinitro-1,3,5-triazacyclohexane or RDX

C_6H_6 - prismane

$C_6H_4(COOH)_2$ - prismane dicarboxylic acid

$C_6H_4(NO_2)_2$ - dinitroprismane

$C_6H_5NO_2$ - nitroprismane

$C_{10}H_{16}$ - adamantane

$C_{12}H_{18}$ - wurtzitane

CL20 - hexanitroisowurtzitane

CSD - United Technologies Chemical Systems Division

CsDN - cesium dinitramide

cyclodimethylenedinitramine - 1,3-dinitro-1,3-diazacyclobutane

DAB - diazidoborane

DDI - dimeryl diisocyanate

DN - dinitramide anion or $N(NO_2)_2^-$

DNNC - 1,3,5,5-tetranitrohexahydropyrimidine

F^- - fluorine anion

FN_3 - fluorine azide

FNT - 1-fluoro-3-nitro-1,2,4-triazole or $C_2HFN_4O_2$

$F^-OF_5^+$ - ionic oxygen hexafluoride

FTIR - Fourier Transform Infrared Spectrometer

GAP - glycidyl azide polymer

HADN - hydroxyammonium dinitramide or $NH_3OH\ N(NO_2)_2$

HAN - hydroxyammonium nitrate

$HB(N_3)_2$ - diazidoborane

HEDM - high energy density matter

HEDMX - suggested name for 1,3-dinitro-1,3-diazacyclobutane or $C_2H_4N_4O_4$

HF - Hartree-Fock

HMX - cyclotetramethylenetetranitramine

HN_3 - hydrogen azide

HN_7 - diazidamine

$HNBN_3$ - imidazidoborane

HNDC - 1,3,3,5,7,7-hexanitro-1,5-diazacyclooctane

$H_2N_4O_4$ - 1,1-dinitrohydrazine or aminodinitramide

$H_4N_4O_4$ - ammonium dinitramide or ADN

$HN(N_3)_2$ - diazidamine

HTPB - hydroxyl terminated polybutadiene

IR - infrared

I_{sp} - specific impulse

LiDN - lithium dinitramide

Li_3H - trilithium hydride

LOX - liquid oxygen

LP-1 - propellant fuel, mainly kerosene

N_3 - azide radical

N_4 - cubane

N_6 - hexazabenzene

N_7 - azidamine

N_7^- - diazidamine anion

N_8 - octaazacubane

N_{10} - triazidamine

NF_5 - nitrogen pentafluoride

NG - nitroglycerin

NH_3 - ammonia

$N(N_3)_2^-$ - diazidamide anion

$N(N_3)_3$ - triazidamine

$N(N_3)_4^+$ - tetraazidammonium cation

$N(NO_2)_2^-$ - dinitramide anion

$N(NO_2)_3$ - trinitramine

$N(NO_2)_4^+$ - tetranitramide cation

$N_2(NO_2)_4$ - tetranitrohydrazine

$(N_2(NO_2)_2)_2$ - tetranitrohydrazine

N_2O_5 - dinitrogen pentoxide

N_4O - nitrosyl azide

N_4O_2 - nitryl azide

N_4O_5 - nitrosyldinitramide

N_4O_6 - trinitramine

$N_5O_2^-$ - dioxopentazolide anion

$N_5O_5^-$ - bis [nitroamino] nitrosylamine anion

N_6O_8 - tetranitrohydrazine

N_7O^+ - diazidonitronium cation

NON_3 - nitrosyl azide

NO_2N_3 - nitryl azide

$NO^+N_3^-$ - ionic nitrosyl azide

$NO_2^+N_3^-$ - ionic nitryl azide

NTO - 3-nitro-1,2,4-triazol-5-one or $C_2H_2N_4O_3$

OF_4 - oxygen tetrafluoride

OF_5^+ - oxypentafluoride cation

OF_6 - oxygen hexafluoride

$ON(N_3)_2^+$ - oxodiazidamide cation

PCN - polycyclic nitramine

PEG - polyethylene glycol

RDX - cyclotrimethylenetrinitramine or 1,3,5-trinitro-1,3,5-triazacyclohexane or $C_3H_6N_6O_6$

RHF - restricted Hartree-Fock

SRI - SRI International

TAA - triazidamine or $N(N_3)_3$

TADB - tetraazidiborane

TNAZ - 1,3,3-trinitroazididine or $C_3H_4N_4O_6$

UTRC - United Technologies Research Center

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1.0 SUMMARY

A theoretical research investigation has been undertaken of high energy chemical species that are attractive candidates for advanced propulsion systems. The tasks of this research program to date have included the following studies: 1) high symmetry and hypervalent structures as advanced oxidizers; 2) azide-like species such as azidamine (N_7) and nitryl azide (NO_2N_3); 3) nitrated cyclic and polycyclic compounds, as further developments of cyclic nitramines such as the cyclotetramethylenetetranitramine (HMX) and polycyclic nitramine (PCN) family of propellants; 4) an extensive analysis of dinitramide compounds as potential chlorine-free oxidizers; 5) nitrated ring structures including nitrozoles and azididines; and 6) substituted prismanes. The significant findings in these six areas of high energy materials are described in the following paragraphs.

Studies of oxygen hexafluoride (OF_6) indicate that this high symmetry structure may exist as a gas phase species exhibiting mainly covalent bonding. However, there is a low transition state barrier for formation of the ionic oxygen hexafluoride ($F^-OF_5^+$) structure, which has low energy content. The chemistry of this compound thus resembles that for nitrogen pentafluoride (NF_5). It may be of interest to study oxygen tetrafluoride (OF_4) and other mixed oxidizers, but the potential for significant specific impulse (I_{sp}) improvement from this class of oxidizers appears to be limited.

All of the new azide-like structures that were examined exhibit very large positive heats of formation. The chemistry of the diazidamide anion parallels that for the dinitramide anion but exhibits much higher energy content. The fundamental problem with azidamines is their low energy barrier for nitrogen elimination. This class of compounds (azides) is chemically interesting, highly energetic, but exhibits limited structural stability, even offering explosive character. Further research in this area is warranted, however, since synthesis techniques for azide-like structures are often applicable to other classes of compounds that exhibit low decomposition barriers.

Nitramine chemistry is presently a dynamic area for synthesis of new compounds. Calculations of hexanitroisowurtzitane (CL20) confirm the structure of this molecule and verify the high positive heat of formation. Based on these studies of CL20, several new polycyclic nitramine structures were analyzed. A second compound of this type can be formed by carbon-bridging on two HMX molecules. Nitrogen-bridging was examined on two cyclotrimethylenetrinitramine (RDX) molecules and a stable pentadecane structure was found: 2,4,6,8,10,12,13,14,15-nonanitra-2,4,6,8,10,12,13,14,15-nonaazatetracyclo $\square$ ($5.5.1.1^{3,11}1^{5,9}$) pentadecane. This is the first polycyclic nitramine that was analyzed that exhibits a positive oxygen balance (+3 O atoms). Synthesis activities on these new polycyclic nitramines appears to be warranted.

Several new compounds, mainly alkali and ammonium salts, were synthesized that exhibit the basic dinitramide anion [$N(NO_2)_2^-$] structure. An extensive study of this new inorganic anion and several new dinitramide compounds was undertaken. Several new compounds were

examined for structural stability including trinitramine [$N(NO_2)_3$] and hydroxyammonium dinitramide [HADN]. This dinitramide group can also be realized by systematic nitration of a starting compound such as hydrazine. Three vibrationally stable compounds: 1,1-dinitrohydrazine, 1,2-dinitrohydrazine and tetranitrohydrazine were found. This last compound should be a leading candidate for synthesis activities of advanced oxidizers.

Studies of nitrated ring structures focused on the structure, stability and energy content of 1,3,3-trinitroazididine [TNAZ]. Beyond TNAZ, calculations were undertaken on several compounds that were suggested or already synthesized by SRI, International (SRI). They include 1-amino-3-nitro-1,2,4-triazole; 1-amino-3,5-dinitro-1,2,4-triazole; 1-fluoro-3-nitro-1,2,4-triazole; and 1-amino-3-nitrotetrazole. Finally, 1,3-dinitro-1,3-diazacyclobutane, which is the smallest member in the RDX, HMX nitramine series was examined. The studies of TNAZ suggested that this compound should exhibit stability. It was found that this compound has a molar heat of formation similar to RDX and surprisingly little strain energy in the ring. The name HEDMX is suggested as an identifier for this new cyclic nitramine, which is a prime target for experimental synthesis.

The last series of compounds that was studied were [n]-prismanes. Calculations indicate that both the nitroprismanes and dinitroprismane structures are stable. Nitration lowers the heat of formation by ~ 10%, but these compounds exhibit high heats of formation (+100 to +125 kcal/mol) in any case, owing to their high strain energy. Further synthesis and compound characterization activities should be encouraged for this class of strained hydrocarbons.

2.0 INTRODUCTION

This report documents the work completed by The United Technologies Research Center (UTRC) on Contract F04611-90-C-0009, "Theoretical Research Investigation of High Energy Chemical Species," for the United States Air Force (USAF) Operating Location (OL-AC) Phillips Laboratory (PL), Propulsion Directorate, Edwards AFB, California. It was intended that the theoretical studies under this contract would be closely coupled with experimental synthesis activities on many of these compounds that were ongoing at SRI International, Rockwell Science Center, Rocketdyne, and Phillips Laboratory. The objectives of this research program were to identify those light element molecular species that have sufficient internal energy to be useful in advanced chemical propulsion systems; to characterize their molecular structure, energy content and structural or radiative stability; to examine the probable kinetic routes for decomposition of these species; to characterize the vibrational and electronic spectra and other static molecular properties; and to propose possible synthesis routes for their formation and subsequent storage.

A goal of this theoretical investigation was to furnish fundamental data and to provide a better understanding of the possibilities of forming chemical compounds that represent advanced high energy sources. It was also intended that this theoretical research effort be carried out with sufficient flexibility to aid in the analysis and guidance of any concurrent experimental programs of synthesis of high energy molecular species. To this end, the tasks of this research program to date have included the following studies: 1) high symmetry and hypervalent structures as advanced oxidizers; 2) azide-like species such as N_7 and NO_2N_3; 3) nitrated cyclic and polycyclic compounds, as further developments of cyclic nitramines such as the HMX and PCN family of propellants; 4) an extensive analysis of dinitramide compounds as potential chlorine-free oxidizers; 5) nitrated ring structures including nitrozoles and azididines; and 6) substituted prismanes.

The research program was formulated in three phases: The first phase was devoted to screening potential advanced propellants in the six groups described above. On the basis of these studies, several candidate species were selected for more accurate calculations and predictions of their thermochemistry. The final phase involved studies of molecular properties of several selected advanced propellant species and an analysis of their potential energy reaction surfaces in regions defining the formation and decomposition of these species.

During the course of this research investigation, several new types of compounds were suggested based on the results of the screening studies. In particular, exploratory studies indicate stability for trinitramine $[N(NO_2)_3]$, and for several salts formed from the tetranitramide cation $[N(NO_2)_4{}^+]$. In addition, preliminary studies indicate stability for tetranitrohydrazine $[N_2(NO_2)_4]$, which has potential as a highly energetic oxidizer material. Exploratory studies also found stability for several [n]-prismane and nitro-prismane compounds. Unsubstituted triprismanes, cubane and pentaprismane structures have been synthesized. Working in collaboration with Dr. Karl Christe, UTRC identified and characterized a class of azide

compounds known as azidimines and carried out further characterization of dinitramide structures. An extensive set of calculations was also carried out on many of the nitrated triazole and pentazole compounds suggested or synthesized by SRI.

In addition to the compounds described above, UTRC's theoretical data on bonding and the relative stability of several new compounds, particularly data derived from various nitramide forms, had suggested a new class of inorganic compounds based on the dinitroboride anion $[B(NO_2)_2^-]$. In preliminary studies, stability was found for these structures which have neither been synthesized or discussed in the extensive literature on boron compounds. Detailed studies of this new class of compounds, however, led to low barriers for rearrangement to unenergetic forms or to decomposition.

The calculated results and pertinent discussion are presented in Section 3. A concluding summary and recommendations based on the results of this program are given in Section 4. Appendix A contains a list of all technical presentations and publications that have resulted from this research program. Abstracts of the pertinent published papers are then collected in Appendix B.

3.0 DISCUSSION OF RESULTS

This research program was divided into studies of molecular species that can be categorized into several groups as follows:

1. high symmetry hypervalent structures,
2. azide-like structures,
3. nitrated cyclic and polycyclic compounds,
4. dinitramide compounds,
5. nitrated ring structures,
6. substituted prismanes.

Detailed reports on many of these studies have been published in the scientific literature, as shown in Appendix A. A brief summary of the calculated results is presented in Sections 3.1 through 3.6, as categorized by the groups listed above in this paragraph.

3.1 High Symmetry Hypervalent Structures (OF_6)

Ab initio calculations of OF_6 were carried out at both the SCF and MP2 levels of theory, using several different basis sets. Calculations were performed using both the Gaussian and CADPAC series of programs, the latter mainly for second derivative analysis at the MP2 level for this closed shell structure. Optimized OF_6 geometries were calculated at the SCF and MP2 levels of theory. Harmonic vibrational frequencies were subsequently computed at the SCF and MP2 stationary points.

Results of the geometry optimization calculations are shown in Table 1. All calculations predict an octahedral structure, O_h. The optimum bond length for OF_6 appears to be only weakly dependent on the chosen basis set at the HF level of theory. However, at the MP2 level of theory, there is a significant lengthening of the bond if diffuse functions are included in the basis set. If the optimum bond length becomes greater than ~ 1.7 Å, depending on the basis, there is one imaginary frequency. Displacement along this mode corresponds to an asymmetric axial stretch leading to dissociation into the fluorine anion (F^-) and the oxypentafluoride cation (OF_5^+) in C_{4v} symmetry. This conformation for OF_5^+ is a saddle corresponding to the Berry pseudorotation state in the $D_{3h} \rightarrow C_{4v} \rightarrow D_{3h}$ ligand interchange process. The calculated energy barrier for the pseudorotation process in OF_5^+ is 6.5 kJ/mol at the HF/6-31G(d) level of theory. This is similar to the calculated barrier of 8.8 kJ/mol for the corresponding process in NF_5. At the HF level of theory, the covalent OF_6 structure is energetically favored. The predicted long bond length at the MP2 level of theory, using diffuse basis functions, results in a reference state which is UHF unstable. Thus, MP2 may not provide an adequate description of the electronic structure of this system where there appears to be a stability competition between the covalent D_{3h} structure and the $OF_5^+F^-$ ion-pair. The stability of OF_6 is therefore similar to that for NF_5. A gas phase species may exist, but the ionic form appears to be favored in the solid.

Table 1. Gradient Optimized Structures and Energies for OF_6

Theory	R(Å)	E(h)	ZPE (h)
HF/6-31G	1.6126	-670.2323 325	0.0168 625
HF/6-31G(d)	1.5407	-670.3343 435	0.0183 033
HF/6-31G(2df)	1.5293	-670.3586 884	---
HF/6-31+G(d)	1.5457	-670.3605 824	0.0177 040
HF/6-311G(d)	1.5470	-670.5047 114	0.0166 128
MP2/6-31G(d)	1.6673	-671.8802 131	0.0128 721
MP2/6-31+G(d)	1.6956	-671.9594 044	---
MP2/6-311G(d)	1.7210	-672.4353 062	*
MP2/6-311+G(d)	1.7452	-672.4817 277	---

* 1 imaginary frequency - asymmetric axial stretch; --- not calculated

3.2 Azide-like Structures

3.2.1 $N(N_3)_3$, $HN(N_3)_2$, $N(N_3)_2^-$ and $N(N_3)_4^+$. The successful synthesis of halogen azides and dinitramide structures has led to an examination of the possibility of stability of other unusual nitrogen structures. Previous theoretical studies have examined the stability of several energetic forms of N_x. N_6 has been shown to be stable as a hexazabenzene structure at the SCF level of theory (Refs. 1-3) but subsequent calculations at a correlated level of theory indicate this conformation to be a second-order saddle point (Refs. 1, 4). Several studies of N_6 as an open chain structure have been reported (Refs. 5, 6). The lowest conformation appears to have C_2 symmetry and exists as a weak dimer of the azide radical. Engelke (Ref. 2) has examined several other conformations for N_6; all appear to lie higher in energy than the open chain diazide form. An experimental study by Vogler, et al. (Ref. 7) postulated that N_6 is formed as a product of an elimination reaction of a diazido platinum complex at low temperatures. No direct evidence for formation of a stable form of N_6 has been reported. Studies of other polyhedral forms of N_x have been reported (Refs. 4, 8-12). Of particular interest is the tetrahedral N_4 structure, since the corresponding P_4 structure is more stable than P_2. Recent calculations (Ref. 4) at a correlated (MBPT-2) level of theory suggest a barrier of approximately 50 kcal/mol for decomposition of N_4. Octaazacubane [N_8] has also been examined at both the SCF and correlated levels of theory (Refs. 4, 8-10). This highly strained molecule is predicted to have a gas phase heat of formation of ~ 470 kcal/mol (Ref. 4) and decomposes to 4 N_2 via a high activation barrier. Unlike cubane, however, N_8 (O_h symmetry) has no convenient intermediate structures such as those found by Eaton, et al. (Refs. 11, 12) for cubane synthesis.

In contrast to the numerous studies of even-membered nitrogen compounds, little has been reported on odd-membered nitrogen structures beyond the azide radical [N_3]. Nguyen, et al.

(Refs. 13, 14) have examined N_5^- as an open chain form, and as pentazene and pentazole structures. The lowest stable conformation appears to be the open chain form, which is a weak van der Waals complex of $N_2 + N_3^-$. The pentazole anion appears stable at the RHF level of theory, lying some 16 kcal/mol above the van der Waals structure. Further studies at a corrected level of theory are needed to better define the relative energetics of these N_5^- conformations.

The next likely candidate for stability among odd-membered nitrogen compounds is the diazidamine anion $[N_7^-]$. This anion could exist as a $N(N\text{-}N_2)_2^-$ structure, similar to the dinitramide anion $[N(NO_2)_2^-]$, or as a $N(N_3)_2^-$ structure with C_2 symmetry formed by the linkage of two azide groups to a central nitrogen atom. Therefore *ab initio* calculations, including electron correlation, were carried out, for both possible conformations. As shown in the next paragraph, the C_2 structure proved to be a stable minimum. UTRC then examined protonation of this structure to form hydrogen diazidamine $[HN(N_3)_2]$, the simplest stable molecule of this anion. Finally, the triazidamine molecule $[N(N_3)_3]$ was examined and a stable C_3 structure was found for this highly energetic molecule.

Ab initio calculations were carried out for N_7^- in both C_2 and C_s symmetries using the Gaussian 92 programs (Ref. 15). Full geometry optimization at the RHF/6-31G(d) level of theory, followed by a calculation of harmonic frequencies, indicated that the $N(N\text{-}N_2)_2^-$ structure was not a vibrationally stable structure (two imaginary vibrational frequencies). However, at this same level of theory, the open chain diazidamine form of N_7^- was found to be stable in C_2 symmetry, exhibiting all real harmonic frequencies. Additional calculations, improving the basis to include diffuse functions and geometry optimization at the MP2 level of theory, were then carried out. The results are given in Tables 2 and 3, respectively, and the stable C_2 conformation is illustrated in Figure 1. At the MP2 correlated level of theory, the central N_1-N_2 bond distance (1.45 Å) is slightly lengthened (0.08 Å) at MP2[6-31+G(d)] over that previously reported for the dinitramide anion. Other known compounds of nitrogen exhibit even larger N-N bond lengths: N_2O_3 (1.86 Å), N_2O_2 (1.78 Å), and N_2H_4 (1.47 Å). The N_2-N_3 and N_3-N_4 bond lengths are typical of those found in hydrogen azide and several halogen azide compounds (Refs. 16, 17). The central bond angle is close to that for sp^3 hybridization on the central nitrogen atom. A CHELPG charge analysis (Ref. 18) indicates an excess (0.41) negative charge on the central nitrogen atom.

Previous studies have indicated a rich structural chemistry for hydrogen dinitramide (Ref. 19). Accordingly, UTRC examined the stability of the simplest diazidamine compound, hydrogen diazidamine. Geometry optimization was carried out at the RHF/6-31G(d) and MP2/6-31G(d) levels of theory. The vibrational analysis reveals the stable C_s structure given in Table 4 and illustrated in Figure 2. We find geometric parameters for $HN(N_3)_2$ that are very similar to those shown in Table 2 for the diazidamide anion $[N(N_3)_2^-]$.

In a parallel fashion, UTRC examined the structural stability of triazidamine, a compound analogous to trinitramine $[N(NO_2)_3]$ that was recently predicted structurally to be at least as stable as dinitrogen pentoxide $[N_2O_5]$. *Ab initio* geometry optimization calculations of $N(N_3)_3$ were first carried out at the RHF/6-31G(d) level of theory. Harmonic frequency calculations

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Table 2. Calculated Energies and Geometries of the Diazidamide Anion [N(N$_3$)$_2{}^-$]

Level of Theory	RHF/6-31G(d)	RHF/6-31+G(d)	MP2/6-31G(d)	MP2/6-31+G(d)
Energy	-380.866 526	-380.893 845	-382.049 745	-382.097 251
Geometry				
R_{12}	1.4180	1.4089	1.4529	1.4425
R_{23}	1.1974	1.1976	1.2465	1.2472
R_{34}	1.1329	1.1310	1.1754	1.1743
$\theta_{2'12}$	101.81	102.70	100.58	101.21
θ_{123}	113.18	112.82	115.69	113.65
θ_{234}	176.56	177.08	170.02	171.50
$dih_{2'123}$	-180.00	-173.72	-150.11	-156.43
dih_{1234}	-180.00	-154.69	-143.95	-137.65

Energies are in hartrees and geometries are in angstroms and degrees.
RHF/6-31G(d) zero-point energy (scaled) = 0.026488.

Table 3. Calculated Harmonic Frequencies for the Diazidamide Anion [N(N$_3$)$_2{}^-$]

Level of Theory		RHF/6-31G(d)	RHF/6-31+G(d)	MP2/6-31G(d)	MP2/6-31+G(d)

Frequencies [IR intensity]   (vibrational frequencies are in cm^{-1} and IR intensities are in km/mol)

		RHF/6-31G(d)	RHF/6-31+G(d)	MP2/6-31G(d)	MP2/6-31+G(d)
ω_1	(B)	56 [5]	74 [8]	35 [3]	44 [6]
ω_2	(A)	72 [0]	107 [0]	63 [0]	85 [0]
ω_3	(A)	140 [1]	145 [0]	150 [1]	145 [0]
ω_4	(B)	278 [24]	282 [23]	218 [25]	227 [23]
ω_5	(A)	459 [4]	465 [5]	396 [0]	379 [0]
ω_6	(B)	526 [33]	492 [30]	385 [12]	326 [13]
ω_7	(A)	523 [0]	510 [0]	425 [0]	408 [0]
ω_8	(A)	622 [4]	629 [2]	610 [7]	593 [2]
ω_9	(B)	799 [118]	796 [159]	743 [60]	737 [4]
ω_{10}	(A)	991 [20]	1001 [16]	914 [4]	911 [1]
ω_{11}	(B)	982 [114]	1024 [173]	869 [47]	899 [78]
ω_{12}	(B)	1421 [7]	1428 [9]	1162 [2]	1159 [2]
ω_{13}	(A)	1473 [7]	1476 [14]	1188 [9]	1184 [21]
ω_{14}	(B)	2318 [2634]	2304 [2970]	2280 [1197]	2255 [1422]
ω_{15}	(A)	2359 [190]	2388 [256]	2291 [14]	2263 [47]
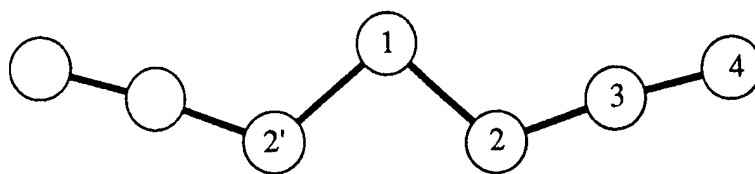
Figure 1

Diazidamide Anion [N(N$_3$)$_2^-$] - C$_2$ Symmetry at the MP2/6-31G(d) Level of Theory

Previous studies have indicated a rich structural chemistry for hydrogen dinitramide (Ref. 19). Accordingly, UTRC examined the stability of the simplest diazidamine compound, hydrogen diazidamine. Geometry optimization was carried out at the RHF/6-31G(d) and MP2/6-31G(d) levels of theory. The vibrational analysis reveals the stable C$_s$ structure given in Table 4 and illustrated in Figure 2. We find geometric parameters for HN(N$_3$)$_2$ that are very similar to those shown in Table 2 for the diazidamide anion [N(N$_3$)$_2^-$].

Table 4. Calculated Energies and Geometries of the Diazidamine Molecule [HN(N$_3$)$_2$]

Level of Theory	RHF/6-31G(d)	MP2/6-31G(d)
Energy (hartrees)	-381.471 597	-382.633 146
Geometry (angstroms and degrees)		
R_{12}	1.4249	1.4665
R_{15}	0.9989	1.0213
R_{23}	1.2508	1.2679
R_{34}	1.0971	1.1563
θ_{215}	104.25	101.16
θ_{123}	108.14	108.39
θ_{234}	173.84	171.29
dih$_{2'152}$	114.89	111.10
dih$_{5123}$	-136.24	-153.03
dih$_{1234}$	-178.19	-173.05

RHF/6-31G(d) zero-point energy (scaled) = 0.041008.

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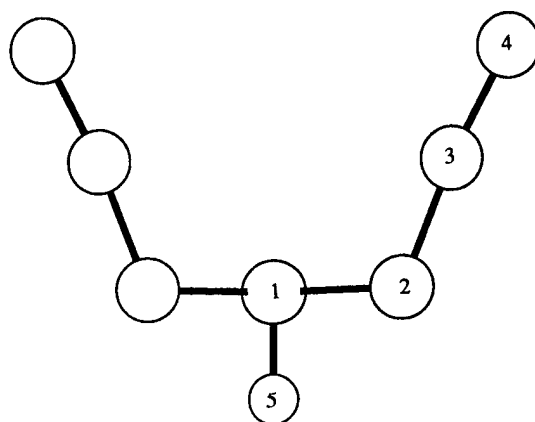
Figure 2

Diazidamine Molecule [HN(N₃)₂] - Cₛ Symmetry at the MP2/6-31G(d) Level of Theory

In a parallel fashion, UTRC examined the structural stability of triazidamine, a compound analogous to trinitramine [N(NO₂)₃] that was recently predicted structurally to be at least as stable as dinitrogen pentoxide [N₂O₅]. *Ab initio* geometry optimization calculations of N(N₃)₃ were first carried out at the RHF/6-31G(d) level of theory. Harmonic frequency calculations confirmed a vibrationally stable C₃ structure, as illustrated in Figure 3.
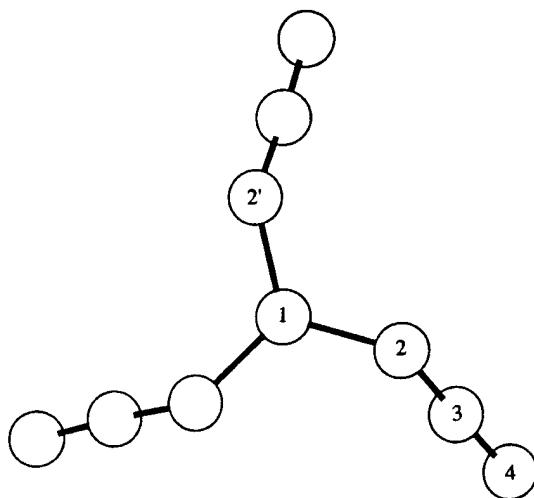
Figure 3

Triazidamine Molecule [N(N₃)₃] - C₃ Symmetry at the RHF/6-31G(d) Level of Theory

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An improved geometry was optimized at the MP2/6-31G(d) level, and again the C_3 structure of $N(N_3)_3$ was found to be vibrationally stable. Inclusion of diffuse functions at the RHF level resulted in only minor changes in predicted bond lengths and angles. The results are summarized in Tables 5 and 6.

Table 5. Calculated Energies and Geometries of the Triazidamine Molecule [$N(N_3)_3$]

Level of Theory	RHF/6-31G(d)	RHF/6-31+G(d)	MP2/6-31G(d)
Energy (hartrees)	-544.061 595	-544.128 121	-545.773 964
Geometry(angstroms and degrees)			
R_{12}	1.4219	1.4206	1.4626
R_{23}	1.2514	1.2515	1.2713
R_{34}	1.0966	1.0961	1.1551
$\theta_{2'12}$	106.57	106.73	103.87
θ_{123}	107.41	107.46	106.46
θ_{234}	174.02	173.94	171.55
$dih_{2'123}$	147.61	150.49	147.30
dih_{1234}	174.65	174.19	177.34

RHF/6-31G(d) zero-point energy (scaled) = 0.042438.

As in ammonia (NH_3), nitrogen trifluoride (NF_3), trimethylamine and trinitramine (Ref. 20), UTRC's calculations show that triazidamine is pyramidal, not planar. The N-N central bond distance is 1.46 Å in $N(N_3)_3$, very close to that found in hydrazine (1.47 Å) and in the diazidamine anion (1.44 Å), and considerably shorter than the corresponding N-N bond distance in trinitramine (1.54 Å). This suggests weak electrostatic interaction between the azide groups in $N(N_3)_3$. In covalent azides, such as hydrogen azide (HN_3) and fluorine azide (FN_3), thermal decomposition occurs by cleavage of the weak N-N double bond:

$$HN_3 \rightarrow N_2 + NH \tag{1}$$

$$FN_3 \rightarrow N_2 + NF \tag{2}$$

The barrier to decomposition is small for HN_3 and ~10.9 kcal/mol for FN_3, much less than the N-H and N-F bond strengths. In $HN(N_3)_2$ and $N(N_3)_3$, the single bond to the central nitrogen is probably much weaker (~40 kcal/mol in nitramides), but still larger than the barrier for:

$$HN(N_3)_2 \rightarrow N_2 + fragments \tag{3}$$

$$N(N_3)_3 \rightarrow N_2 + fragments \tag{4}$$

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Table 6. Calculated Harmonic Frequencies for the Triazidamine Molecule [N(N$_3$)$_3$]

Level of Theory	RHF/6-31G(d)		RHF/6-31G(d)		MP2/6-31G(d)	

Frequencies [IR intensity] (Vibrational frequencies are in cm^{-1} and IR intensities are in km/mol)

		RHF/6-31G(d)		RHF/6-31G(d)		MP2/6-31G(d)	
ω_1	(E)	36	[1]	39	[1]	19	[0]
ω_2	(E)	36	[1]	39	[1]	19	[0]
ω_3	(A)	52	[0]	59	[1]	35	[0]
ω_4	(A)	155	[0]	164	[0]	129	[0]
ω_5	(E)	252	[2]	251	[2]	212	[1]
ω_6	(E)	252	[2]	251	[2]	212	[1]
ω_7	(E)	468	[12]	466	[11]	413	[6]
ω_8	(E)	468	[12]	466	[11]	413	[6]
ω_9	(A)	536	[15]	539	[15]	486	[3]
ω_{10}	(A)	593	[0]	592	[0]	524	[0]
ω_{11}	(E)	644	[16]	626	[13]	526	[2]
ω_{12}	(E)	644	[16]	626	[13]	526	[2]
ω_{13}	(A)	649	[1]	635	[0]	549	[0]
ω_{14}	(E)	796	[13]	793	[12]	713	[24]
ω_{15}	(E)	796	[13]	793	[12]	713	[24]
ω_{16}	(E)	1130	[23]	1129	[39]	897	[83]
ω_{17}	(E)	1130	[23]	1129	[39]	897	[83]
ω_{18}	(A)	1109	[4]	1098	[5]	931	[0]
ω_{19}	(E)	1217	[314]	1220	[321]	1171	[94]
ω_{20}	(E)	1217	[314]	1220	[321]	1171	[94]
ω_{21}	(A)	1276	[107]	1272	[126]	1221	[15]
ω_{22}	(E)	2457	[739]	2454	[771]	2380	[375]
ω_{23}	(E)	2457	[739]	2454	[771]	2380	[375]
ω_{24}	(A)	2490	[403]	2485	[445]	2387	[103]

Previous calculations on FN$_3$ have shown that the experimentally observed barrier (11.5 kcal/mol) for reaction (2) is well reproduced at the RHF/6-31G(d) level of theory. Gradient optimized transition states for reactions (3) and (4) have been located at the RHF/6-31G(d) level, and the barriers to the decomposition processes (3) and (4) are 9.9 and 10.8 kcal/mol, respectively. The preliminary conclusion is that the shock sensitivity of HN(N$_3$)$_2$ and N(N$_3$)$_3$ may be comparable to that of fluorine azide.

To complete the structural possibilities of polyazamides, the tetraazidammonium cation [N(N$_3$)$_4$$^+$] was also examined. *Ab initio* geometry calculations were carried out at the RHF/6-31G(d) level of theory. A harmonic frequency analysis indicated a vibrationally stable D$_{2d}$ structure, as illustrated in Figure 4. An improved optimized geometry was then found at the MP2/6-31G(d) level of theory. The calculated geometries and harmonic frequencies are shown in Tables 7 and 8, respectively.

Figure 4

Tetraazidammonium Cation [N(N$_3$)$_4$$^+$] - D$_{2d}$ Symmetry at MP2/6-31G(d) Level of Theory
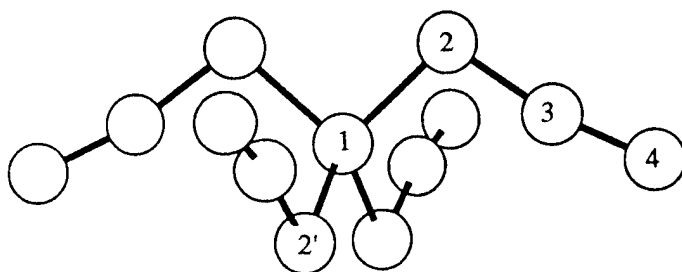
Table 7. Calculated Energies and Geometries of the Tetraazidammonium Cation [N(N$_3$)$_4$$^+$]

Level of Theory	RHF/6-31G(d)	MP2/6-31G(d)
Energy (hartrees)	-707.070 221	-709.216 858
Geometry (angstroms and degrees)		
R$_{12}$	1.4359	1.4651
R$_{23}$	1.2929	1.2919
R$_{34}$	1.0850	1.1489
θ$_{2'12}$	100.08	99.15
θ$_{123}$	106.81	106.05
θ$_{234}$	171.75	169.88

RHF/6-31G(d) zero-point energy (scaled) = 0.055930.

Table 8. Calculated Harmonic Frequencies for the Tetraazidammonium Cation [N(N$_3$)$_4$$^+$]

RHF/6-31G(d) Level of Theory

A1:   113 [0], 348 [0], 547 [0], 943 [0], 1112 [0], 2599 [0]
A2:   118 [0], 582 [0]
B1:   82 [0], 423 [0], 614 [0]
B2:   163 [0], 443 [6], 592 [1], 1074 [26], 1231 [1], 2589 [52]
E: 87 [2], 226 [3], 473 [11], 615 [39], 842 [49], 965 [96], 1161 [231], 2589 [292]

Vibrational frequencies are in cm^{-1} and IR intensities [ ] are in km/mol.

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Comparing the geometries of the tetraazidammonium cation with that found for the neutral triazidamine molecule, we find nearly identical N-N bond lengths to the central nitrogen atom at both the RHF and MP2 level of theory. This indicates that there is little additional electrostatic repulsion (crowding) resulting from the added N_3^+ group in the cation. Similarly, the central and end nitrogen atom bond lengths in the azide groups do not significantly differ between the neutral triazidamine and tetraazidammonium cation structure.

The heat of formation of $HN(N_3)_2$ can be extracted from the enthalpy change for the isogyric reaction:

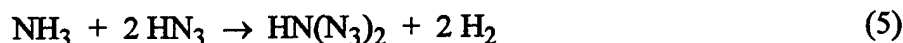$$NH_3 + 2\,HN_3 \rightarrow HN(N_3)_2 + 2\,H_2 \qquad (5)$$

Using a calculated heat of reaction of 64.6 kcal/mol at the MP2/6-31G(d) level of theory for reaction (5) and the experimental heats of formation of NH_3 and HN_3 (Ref. 21), ΔH_f^0 (0 K) = +198.9 kcal/mol for $HN(N_3)_3$.

The heat of formation of $N(N_3)_3$ can be estimated from the heat of reaction for

$$5\,N_2 \rightarrow N_{10} \qquad (6)$$

or, alternatively, from the isogyric reaction

$$NH_3 + 3\,HN_3 \rightarrow N(N_3)_3 + 3\,H_2 \qquad (7)$$

For reaction (7), the heat of formation of triazidamine was estimated from the calculated MP2/6-31G(d) heat of reaction and the experimental heats of formation of HN_3 and NH_3 (Ref. 21). The results are summarized in Table 9, which indicates that $N(N_3)_3$ represents a very energetic and possibly explosive material, ΔH_f^0 $(N(N_3)_3)$ = +298 kcal/mol. This energy content arises, however, from the large difference in the N-N single and double strengths compared to that of the triple bond, rather than as the strain energy that arises in a structure such as octaazacubane. Further, the building block for this molecule is the diazidamine anion, which may possibly be synthesized starting from dimethylamine.

Table 9. Calculated Heat of Formation for the
Diazidamine [$HN(N_3)_2$] and Triazidamine [$N(N_3)_3$] Molecules

MP2/6-31G(d) Level of Theory

Reaction		Equation	ΔH_f^0(0 K)
$HN(N_3)_2$:	$NH_3 + 2\,HN_3 \rightarrow HN(N_3)_2 + 2\,H_2$	(5)	198.9 kcal/mol
$N(N_3)_3$:	$NH_3 + 3\,HN_3 \rightarrow N(N_3)_3 + 3\,H_2$	(7)	298.1 kcal/mol

3.2.2 NON₃ and NO₂N₃. Calculations on several nitro azides were carried out. Klapötke and coworkers (Ref. 22) have recently reported the synthesis of nitrosyl azide [NO⁺N₃⁻]. This energetic compound is stable at low temperatures, existing as a chain-type structure rather than as a cyclic form. Calculations for NO⁺N₃⁻ and for NO₂⁺N₃⁻ (nitryl azide) were carried out at the MP2/6-31+G(d) level of theory. The optimized structures (both planar) are shown in Figures 5 and 6, respectively.
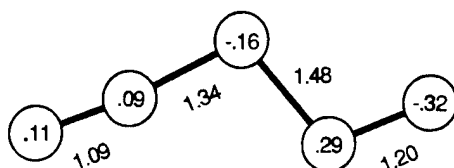
Figure 5
Nitrosyl Azide [NO⁺N₃⁻]
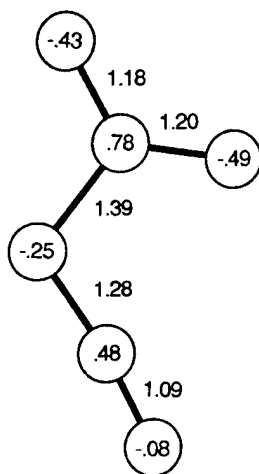
Figure 6
Nitryl Azide [NO₂⁺N₃⁻]

It is of interest to compare the relative value of several oxidizers, including the nitro azides, in improving the performance characteristics of solid propellant formulations. Heats of formation for all of these compounds have been calculated at the MP2/6-31+G(d) level of theory from isodesmic reactions. The use of isodesmic reactions permits cancellation of errors that can otherwise accumulate if heats of formation are based on atomization energies. Solid densities were estimated using Cady's method (Ref. 23) for evaluating explosives. These calculated data are shown in Table 10.

Table 10. Thermochemistry of Advanced Propellants

Compound	Formula	Mol. Wt.	Density gm/cm^3	ΔH_f(25°C) kcal/mol
Triprismane	C_6H_6	78.12	1.29	+134.7
Nitrotriprismane	$C_6H_5NO_2$	123.11	1.55	+125.3
Dinitrotriprismane	$C_6H_4(NO_2)_2$	168.11	1.71	+121.5
Tetranitrohydrazine	$N_2(NO_2)_4$	212.04	2.17	+140.0
Trinitramine	$N(NO_2)_3$	152.02	2.15	+90.0
Diazidamine	$HN(N_3)_2$	99.06	1.56	+199.0
Triazidamine	$N(N_3)_3$	140.07	1.58	+302.0
Diazidoborane	$HB(N_3)_2$	95.86	1.52	+108.0
Imidazidoborane	$HNBN_3$	67.85	1.34	+56.0
Nitrosyl azide	NON_3	72.03	1.54	+105.0
Nitryl azide	NO_2N_3	88.03	1.76	+90.0
3-nitro-1,2,4-triazol-5-one (NTO)	$C_2H_2N_4O_3$	130.06	1.75	-3.2
1-amino-3-nitro-1,2,4-triazol	$C_2H_3N_5O_2$	129.08	1.61	+55.6

Density is calculated by the method of Cady (Ref. 23).

The new energetic materials are separated into three groups: oxidizers, monopropellants, and oxygen-deficient energetic materials. These compounds are formulated in propellants and the I_{sp}'s of these propellants are calculated through the AFPL theoretical I_{sp} program. The oxidizers are calculated as ammonium dinitramide (ADN) substitutes in an ammonium dinitramide/glycidyl azide polymer (ADN/GAP) smokeless propellant. The monopropellants replace HMX in a smokeless/PEG (polyethylene glycol) propellant. The oxygen-deficient materials are formulated in an aluminized/HTPB (hydroxyl terminated polybutadiene) propellant as replacements for HMX.

Oxidizers. Tetranitrohydrazine [$N_2(NO_2)_4$], trinitramine, nitrosyl azide, and nitryl azide are the oxidizers formulated in a GAP/smokeless propellant. The calculated I_{sp}'s are shown in Table 11. An average of 30 to 40 sec improvement in the specific impulse over the formulation containing ADN as an oxidizer is achieved. Similar improvement is also seen in density I_{sp}. The large improvement in performance also comes with much lower percentages of oxidizer contents. Lower solid contents make propellant processing easier. Lower solid contents also produce propellants with better physical properties.

Monopropellants. Triazidamine (TAA), a monopropellant, is used in replacement of HMX, also a monopropellant, in a selected formulation. A generic energetic smokeless/PEG formulation is chosen for comparison. The base formula is not optimized. This base formulation contains HMX (60 %), PEG (13 %), NG (nitroglycerin) (25 %), and N-3200 (2 %). As shown in Table 11, a 50 sec improvement in I_{sp} is achieved.

Oxygen-Deficient Energetic Materials. Diazidoborane [$HB(N_3)_2$], imidazidoborane [$HNBN_3$], 1-amino-3-nitro-1,2,4-triazol [$C_2H_3N_5O_2$], and the two nitrotriprismanes are oxygen-deficient energetic materials. A good way has not yet been found to incorporate these materials into existing propellant formulations for a quick performance comparison. For now, an aluminized/HTPB system is chosen as a base propellant. The propellant has the following formulation: HTPB (8.25 %), DDI (dimeryl diisocyanate) (1.25 %), aluminum (20 %), AP (58 %), and HMX (12 %). Again, this generic formulation is used for comparison only and is not optimized. Diazidoborane and 1-amino-3-nitro-1,2,4-triazol are used to replace HMX in the base formula. The percentages of aluminum and AP are adjusted to maximize the calculated performance. Table 11 lists the calculated results. UTRC believes that an improvement in performance can be realized upon finding a suitable propellant.

Table 11. Theoretical Performance Characteristics (I_{sp}) of Advanced Propellants

Oxidizers

Ingredient	I_{sp}, sec	I_{sp} (vac)	I_{sp}*Density	I_{sp}(vac)*Density	Density	% Oxidizer
AP	255	277	16.2	17.5	1.75	78
ADN	265	287	16.2	17.6	1.69	83
$N_2(NO_2)_4$	293	320	18.6	20.3	1.75	62
$N(NO_2)_3$	293	319	18.2	19.9	1.71	64
NON_3	305	331	16.4	17.8	1.48	81
NO_2N_3	294	319	17.1	18.6	1.61	74

Monopropellants

Ingredient	I_{sp},sec	I_{sp} (vac)	I_{sp}*Density	I_{sp} (vac)*Density	Density
HMX (base)	243	261	14.7	15.8	1.67
TAA	296	318	16.2	17.4	1.51

Oxygen-Deficient Energetic Materials

Ingredient	I_{sp}, sec	I_{sp} (vac)	I_{sp}*Density	I_{sp} (vac)*Density	Density
HMX (base)	266	291	17.7	19.3	1.84
ANT	265	291	17.2	18.9	1.79
DAB	266	291	17.0	18.7	1.76

3.2.3 ON(N₃)₂⁺. Calculations were initiated on the oxodiazidamide cation $[ON(N_3)_2^+]$ following a suggestion by Jeff Bottaro (SRI) that this species might exhibit stability. A vibrationally stable structure has been located at both the HF/6-31G(d) and MP2/6-31G(d) levels of theory. This structure exhibits C_2 symmetry similar to the diazidamide anion. The optimum structure at the HF/6-31G(d) level is shown in Table 12. The calculated vibrational frequencies are given in Table 13. A pictorial representation of this new cation is shown in Figure 7.

Table 12. Calculated Geometry of the Oxodiazidamide Cation $[ON(N_3)_2^+]$
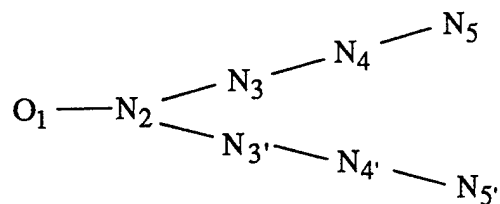
Geometry is in angstroms and degrees

R_{12}	R_{23}	R_{34}	R_{45}	θ_{123}	θ_{234}	θ_{345}	τ_{1234}	τ_{2345}
1.150	1.365	1.305	1.083	117.54	110.37	169.17	142.51	188.58

Table 13. Calculated Harmonic Frequencies and Infrared Intensities for $ON(N_3)_2^+$

Frequencies are in cm⁻¹ and IR intensities [ ] are in km/mol

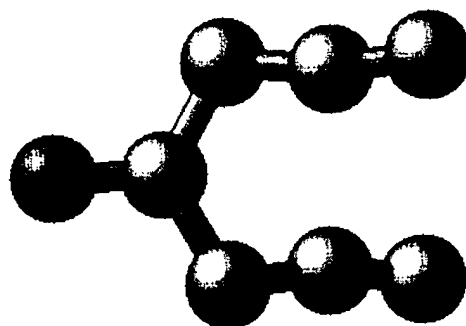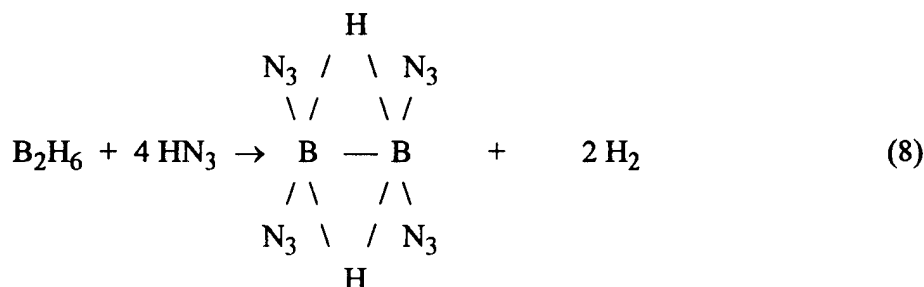| Mode	Frequency		Mode	Frequency	
B	71.2	[2]	A	87.7	[2]
	230.7	[3]		189.8	[3]
	545.0	[8]		459.7	[0]
	572.2	[8]		561.9	[30]
	626.5	[1]		745.8	[1]
	874.1	[46]		881.6	[1]
	1042.8	[53]		1118.1	[264]
	1285.7	[264]		2005.5	[380]
	2626.9	[74]		2636.0	[94]

18

Figure 7
Optimized Structure of the Oxodiazidamide Cation [ON(N$_3$)$_2$$^+$]

3.2.4 Azidoboranes. *Ab initio* calculations were carried out on several azidoborane structures. Wiberg and Michaud (Ref. 24) have shown that HN$_3$ and diborane (B$_2$H$_6$) react in ether by abstracting H$_2$ to form azidoboranes. The gas phase reaction could proceed as

$$
\begin{array}{c}
H \\
N_3 \; / \; \backslash \; N_3 \\
\backslash \, / \quad \backslash \, / \\
B_2H_6 + 4\,HN_3 \rightarrow \quad B \; - \; B \quad + \quad 2\,H_2 \qquad (8) \\
/\,\backslash \quad /\,\backslash \\
N_3 \; \backslash \; / \; N_3 \\
H
\end{array}
$$

provided the reaction products are stable. *Ab initio* calculations were performed to explore the possible existence and stability of the tetraazidoborane (TADB) structure suggested in reaction (8). The RHF/6-31G(d) optimized geometry for TADB is shown in Table 14, and the calculated vibrational frequencies and intensities, which can be used to characterize experimental absorption bands, are given in Table 15. The calculations indicate the likely existence of a vibrationally stable D$_2$ structure for TADB. Calculated heats of reaction and heats of formation are reported in Table 16. These structures include vibrational zero-point corrections obtained from the calculated vibrational frequencies (scaled by 0.8929). The MP2/6-31G(d)//RHF/6-31G(d) heat of formation of TADB, given in Table 16, indicates that reaction (8) is exothermic by 73.2 kcal/mol.

Table 14. Calculated Geometries for Several Azidoborane Structures

RHF/6-31G(d) Level of Theory
Geometries are in angstroms and degrees

Tetraazidoborane TADB (D$_2$)		Diazidoborane DAB (C$_{2v}$)		Imidazidoborane HNBN$_3$ (C$_s$)	
B-B	1.821	H-B	1.179	H-N	0.980
H-B	1.332	B-N$_1$	1.439	N-B	1.225
B-N$_1$	1.464	N$_1$-N$_2$	1.237	B-N$_1$	1.409
N$_1$-N$_2$	1.230	N$_2$-N$_3$	1.095	N$_1$-N$_2$	1.233
N$_2$-N$_3$	1.097	H-B-N$_1$	115.4	N$_2$-N$_3$	1.094
H-B-N$_1$	103.5	B-N$_1$-N$_2$	123.6	H-N-B	180.0
B-N$_1$-N$_2$	118.8	N$_1$-N$_2$-N$_3$	173.1	N-B-H$_1$	177.4
N$_1$-N$_2$-N$_3$	174.7			B-N$_1$-N$_2$	120.1
H-B-N$_1$-N$_2$	-168.2			N$_1$-N$_2$-N$_3$	173.9
B-N$_1$-N$_2$-N$_3$	-179.5			N-B-N$_1$-N$_2$	180.0

Table 15. Calculated Vibrational Frequencies and Intensities for Several Azidoborane Structures

RHF/6-31(d) Level of Theory
Frequencies are in cm^{-1} and intensities [ ] are in km/mol

DAB Diazidoborane

A$_1$ 2845[162], 2588[924], 1401[556], 919[16], 824[81], 506[10], 122[0]

A$_2$ 674[0], 60[0]

B$_1$ 952[59], 686[63], 311[3]

B$_2$ 2532[194], 1435[900], 1279[13], 1043[27], 693[1], 181[0]

TADB Tetraazidoborane

A   2580[0], 2260[0], 1442[0], 1103[0], 835[0], 674[0], 532[0], 2622[0], 186[0], 79[0], 42[0]

B$_1$ 2533[633], 2003[106], 1442[262], 1158[18], 730[47], 668[33], 497[25], 315[1], 155[3], 34[1]

B$_2$ 2537[440], 1744[4], 1450[843], 1312[385], 1080[90], 724[1], 667[8], 453[0], 181[0], 110[1], 33[0]

B$_3$ 2560[2145], 1831[2335], 1357[3117], 1160[391], 877[659], 800[368], 668[90], 485[15], 134[10], 48[2]

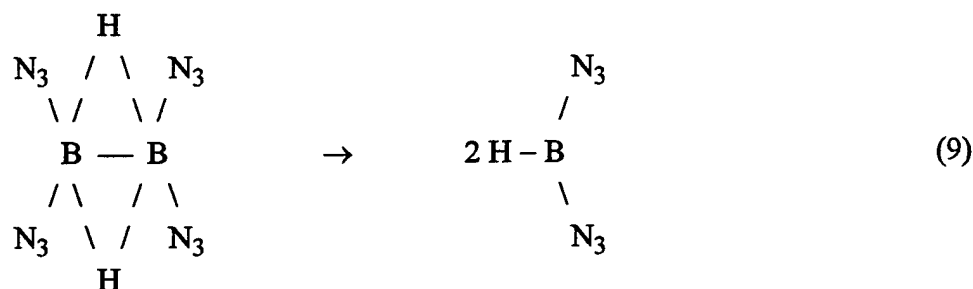**HNBN$_3$ Imidazidoborane**

A'   4146[336], 2592[728], 2178[882], 1432[300], 900[30], 695[11], 559[154], 517[19], 153[0]

A"   651[19], 490[0], 435[210]

Table 16. Calculated Energies and Thermochemistry for Several Azidoborane Structures
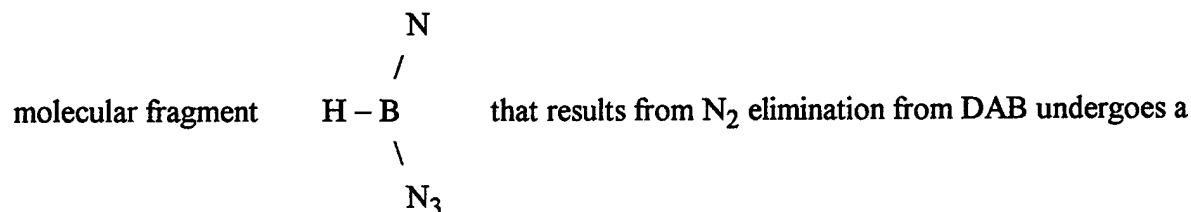
Level of Theory	E(hartrees)	ΔH_r (kcal/mol)	ΔH_f (0 K)(kcal/mol)
TABD Tetraazidoborane (See Eq. 8)			
RHF/6-31G(d)	-703.68903	-33.3	266.2
MP2/6-31G(d)//RHF/6-31G(d)	-705.83842	-75.0	224.5
MP2/6-31+G(d)//RHF/6-31G(d)	-705.87845	-73.2	226.3
DAB Diazidoborane (See Eq. 9)			
RHF/6-31G(d)	-351.86757	-31.0	117.6
MP2/6-31G(d)//RHF/6-31G(d)	-352.92725	-12.2	106.2
MP2/6-31+G(d)//RHF/6-31G(d)	-352.94539	-9.8	108.3
HNBN$_3$ Imidazidoborane (See Eq. 10)			
RHF/6-31G(d)	-243.01229	-57.6	40.4
MP2/6-31G(d)//RHF/6-31G(d)	-243.73651	-38.0	60.0
MP2/6-31+G(d)//RHF/6-31G(d)	-243.75290	-41.1	56.9

In a fashion similar to B_2H_6, TADB can dissociate upon heating, yielding diazidoborane (DAB):

```
               H
      N3  / \  N3                        N3
        \ /  \ /                         /
         B — B          →        2 H – B              (9)
        / \  / \                         \
      N3  \ /  N3                        N3
           H
```
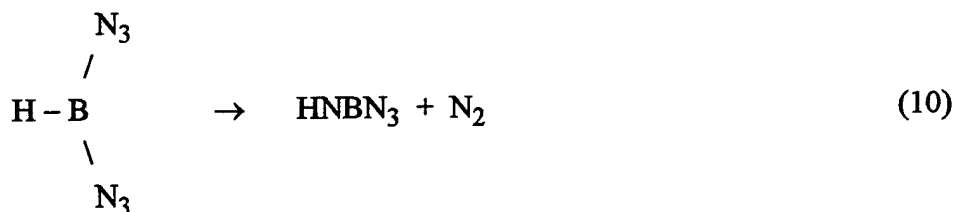
Ab initio calculations of diazidoborane indicate a vibrationally stable C_{2v} structure as shown in Tables 14 and 15. The calculated energies in Table 16 indicate that reaction (9) is exothermic by about 9.8 kcal/mol.

DAB, like the halogen azides, can eliminate a terminal N_2 group. Calculations at the RHF/6-31G(d) level of theory indicate that the barrier for N_2 elimination is 17.9 kcal/mol, a value slightly greater than that found for FN_3 (10.8 kcal/mol calc., 13.6 kcal/mol exp.). The

```
                    N
                   /
molecular fragment     H – B     that results from N2 elimination from DAB undergoes a
                   \
                    N3
```

conformational change by migration of the lone N atom away from the N_3 group and insertion into the H-N bond to form a planar imidazidoborane (HNBN$_3$) structure. Calculations at the RHF/6-31G(d) level of theory, shown in Tables 14 and 15, indicate that this compound is vibrationally stable. The overall reaction

$$
\begin{array}{c}
N_3 \\
/ \\
H - B \qquad \rightarrow \quad HNBN_3 + N_2 \\
\backslash \\
N_3
\end{array}
\qquad (10)
$$

is exothermic by 41.1 kcal/mol, as calculated from the data in Table 16.

3.3 Nitrated Cyclic and Polycyclic Compounds

Calculations were initiated on several new cyclic and polycyclic compounds that appear to have potential in solid rocket propellant formulations. These compounds are new developments in the chemistry of nitramines. Cyclic nitramines such as RDX and HMX have been known for years and were utilized as explosives during World War II. Mixtures of HMX and ammonium perchlorate containing up to 70% HMX have been fired in demonstration motors at United Technologies Chemical Systems Division (CSD). Renewed interest in nitramines centers around the development of caged polycyclic structures. Starting from ring structures such as RDX, HMX or a general alcane ($C_{m+n}H_{2m+n}$), nitramine caged structures can be synthesized by forming C-C bridges between the rings of two or more alcanes. Thus, adamantane ($C_{10}H_{16}$) and wurtzitane ($C_{12}H_{18}$) can be formed from bridging five-member and six-member rings, respectively. Subsequent nitration leads to very energetic forms of these caged molecules.

3.3.1 RDX and HMX. A study of polycyclic caged nitramines was initiated, using RDX and HMX as prototype systems for evaluation and calibration of the computational approaches. Many of the molecules investigated were too large for applications of *ab initio* techniques. Therefore, semi-empirical methods such as AM1 were compared with *ab initio* Hartree-Fock calculations for the smaller systems in order to gain some confidence in the reliability of the semi-empirical predictions. The first system examined was RDX in both the boat and chair structures. The optimized *ab initio* and AM1 structures for the chair form are compared in Figure 8. UTRC's calculated bond lengths and angles are in good agreement with the data compiled by Rogers (Ref. 25). The AM1 predictions are very close to the optimized HF/STO-3G *ab initio* structure. AM1 bond lengths are within 0.05 Å and AM1 bond angles are within 3% of the *ab initio* results.

The second system examined was HMX where only the crown (C_{4v}) structure was examined. Again the AM1 predicted structure is very close to that obtained from a very lengthy HF/STO-3G calculation.
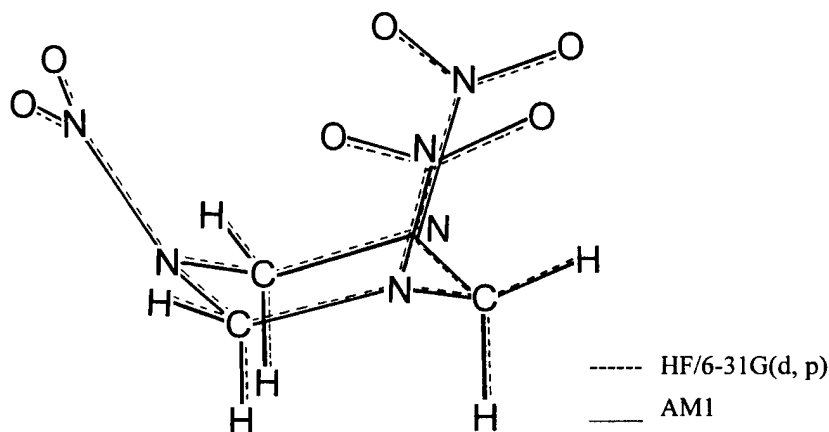

------ HF/6-31G(d, p)

_____ AM1

Figure 8
Comparison of HF/6-31G(d, p) and AM1 Structure for RDX (chair)

3.3.2 CL20. Based on observations that AM1 predicted reliable geometries for RDX and HMX, a study was undertaken of polycyclic caged structures, beginning with the six-carbon isowurtzitane structure [CL20]. In order to further verify the reliability of AM1 predicted structures, both *ab initio* and AM1 optimized structures were calculated for the zeta [C_{2v}] form of hexanitrohexaazaisowurtzitane, a polycyclic nitramine (PCN) sometimes referred to as CL20. The *ab initio* calculations were carried out at the HF/STO-3G level of theory, and the AM1 method employs the STO-3G basis for describing the valence shell. The structures are compared in Figure 9, where some small (<5°) deviations can be seen in the predicted bond angles for the nitro groups, but there is overall excellent agreement between the *ab initio* and semi-empirical predictions. This is a 36-atom molecule and represents the practical limit in the size of the PCN structures that were planned to be investigated. The less symmetric conformations of this PCN were located using the AM1 method. They are shown in Figure 10 for the zeta [C_{2v}] and epsilon [C_s] forms. These conformations do not necessarily correspond one-to-one with the observed polymorphs. In particular, it is known that the alpha phase of CL20 has a non-characteristic infrared (IR) spectra indicating a solid rearrangement or possibly a hydrated form. A companion of UTRC's calculated IR spectra for the C_{2v} form of CL20 with the experimental spectra reported by Yuxiang, et al. (Ref. 26) is shown in Figures 11 and 12, respectively. It is clear that the primary features corresponding to nitro groups are well represented by these calculations.
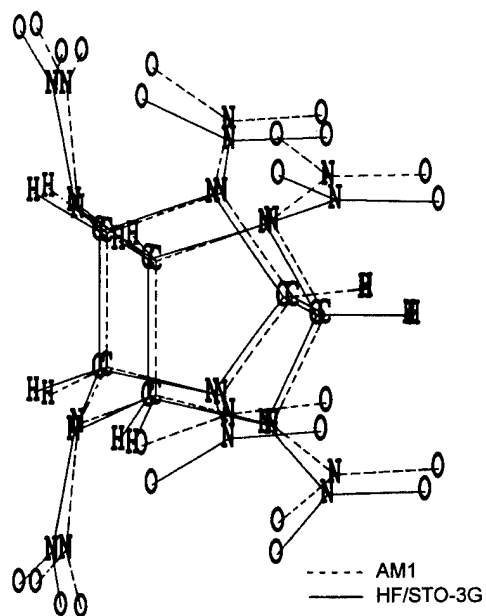
Figure 9
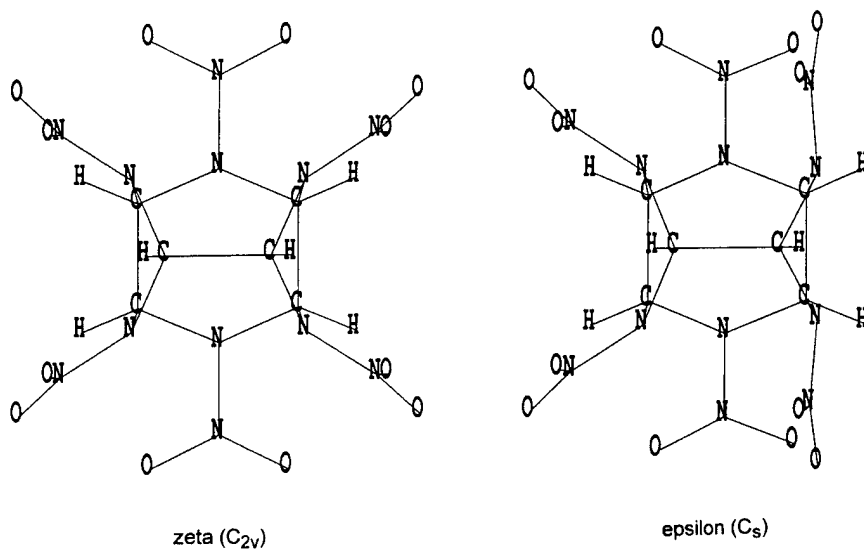**Comparison of the Predicted Structure of the Zeta Form of Isowurtzitane**

zeta (C₂ᵥ)   epsilon (Cₛ)

Figure 10
Comparison of the Zeta and Epsilon Forms of Isowurtzitane Using AM1 Theory
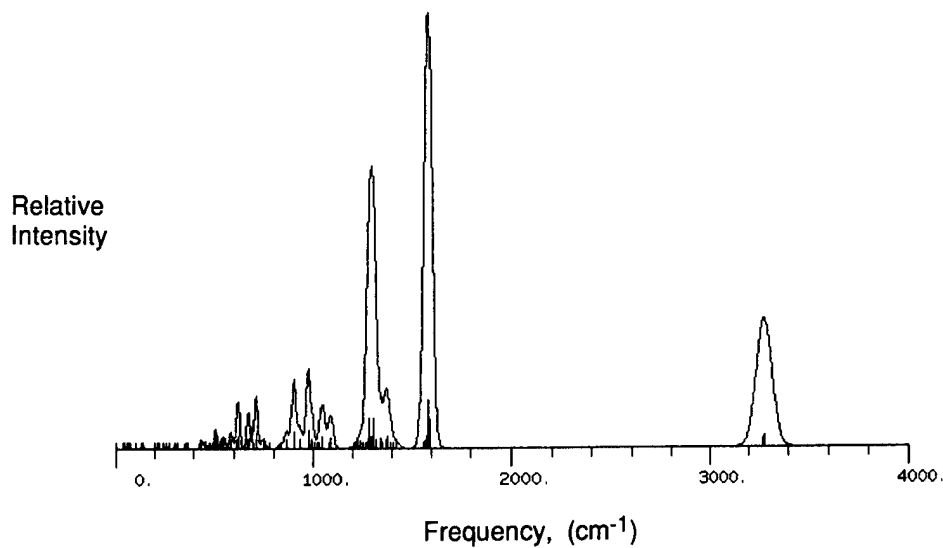
24

Figure 11

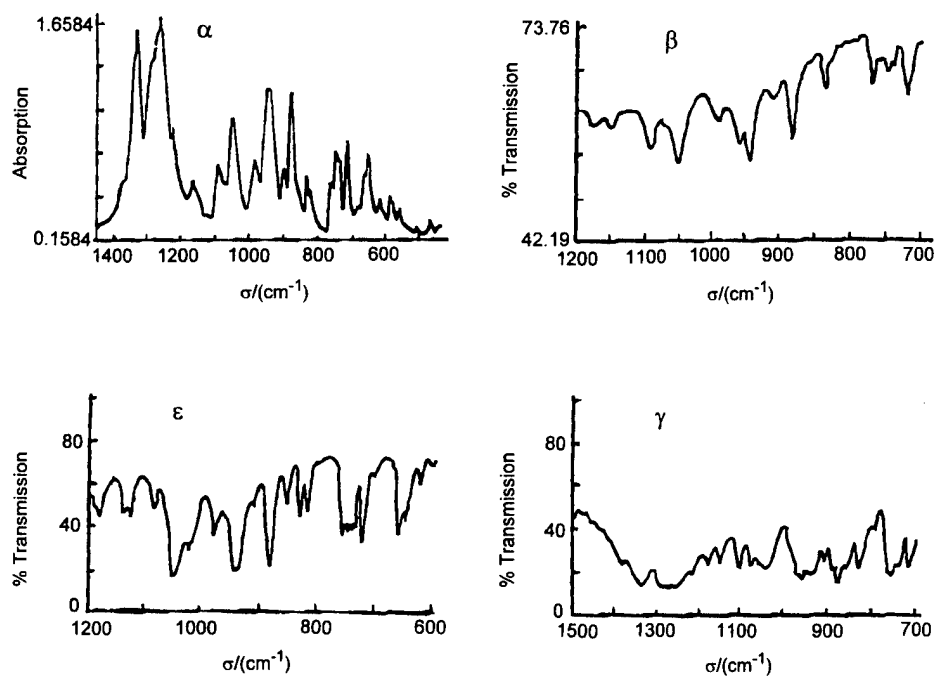**Calculated IR Spectrum for PCN/CL20 - C_{2v} Form (HF/STO-3G Level of Theory)**

Figure 12

FTIR Spectra of Four Polymorphs of CL20

3.3.3 New PCNs.
Based on the success of the AM1 method in describing CL20, the structure of several new polycyclic nitramine (PCN) compounds were analyzed at the AM1 level of theory. The molecules under study are illustrated in Figure 13. The first PCN structure is representative of carbon-bridging on two RDX molecules. There is a vibrationally stable structure in C_s symmetry. This compound would have an oxygen balance of -3 O atoms. The second PCN structure, shown in Figure 13, is representative of carbon-bridging on two HMX molecules. Again, there is a vibrationally stable structure in C_s symmetry. The compound would have an oxygen balance of -4 O atoms. Next, a nitramine group addition was tried across the C-C brigeheads in CL20. This results in the third compound illustrated in Figure 13, which exhibits exceptional vibrational stability. This is the first polycyclic nitramine that has a positive oxygen balance of +3 O atoms. Its thermal stability is unknown, but several synthesis routes are under discussion at CSD. A laboratory synthesis program seems to be warranted for this compound.
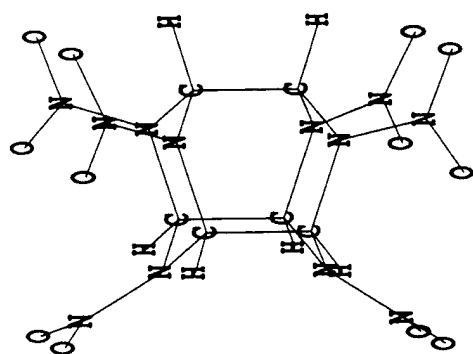
3.4 Dinitramide Compounds

Recently, Bottaro and Schmitt[1] have synthesized several new compounds that exhibit a dinitramide anion structure. These compounds form as salts similar to ammonium nitrate or ammonium perchlorate, rather than as the less stable organic alkyldinitramines (Ref. 27). UTRC has examined the structure of this new inorganic anion and reported estimates of its vibrational spectra and thermodynamic stability. The dinitramide anion exhibits exceptional stability, and several new members of the inorganic dinitramide family have been examined for structural stability and energy content. *Ab initio* calculations were carried out for several new dinitramide oxidizers at the HF/6-31G(d) and MP2/6-31G(d) levels of theory.

3.4.1 DN.
The structure of the dinitramide anion has been studied at both the HF and MP2 levels of theory. The structure of the anion is illustrated in Figure 14, where calculated bond lengths and angles are compared with data derived by Gilardi[2] from X-ray analysis of ADN. A comparison of the calculated IR features for the dinitramide anion with data taken on the cesium salt is shown in Figure 15. The most prominent feature is the new $N-N-NO_2$ rock motion at ~766 cm^{-1} which characterizes this species. The dinitramide anion has C_2 symmetry, and this symmetry is preserved when forming an alkali salt such as lithium dinitramide (LiDN) or cesium dinitramide (CsDN).
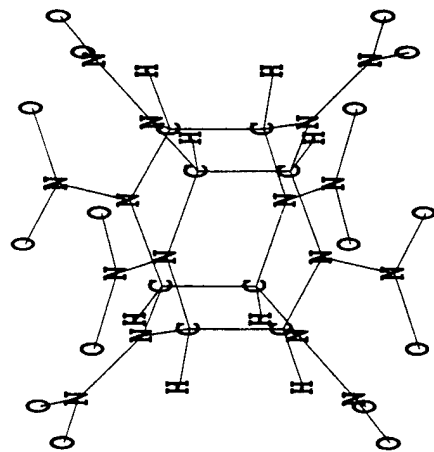
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[1] Schmitt, R. J. and Bottaro, J. C.: private communication, SRI International, 1992.
[2] Gilardi: private communication, Naval Research Laboratory, 1992.

3,5,8,10,11,12-hexanitro-3,5,8,10,11,12-hexaaza-
tetracyclo ☐ (5.3.1.1.2,60.4,9) dodecane

(Carbon-bridging on 2 RDX molecules)

3,5,7,10,12,14,15,16-octanitro-3,5,7,10,12,14,15,16-octaaza-
pentacyclo ☐ (7.5.1.1.3,80.4,130.6,11) hexadecane

(carbon-bridging on 2 HMX molecules)

2,4,6,8,10,12,13,14,15-nonanitra-2,4,6,8,10,12,13,14,15-nonaaza-
tetracyclo ☐ (5.5.1.1.3,111.5,9) pentadecane

(nitrogen - bridging on 2 RDX molecules)

Figure 13
New PCN Structures

( ) - RHF/6-31+G(d)

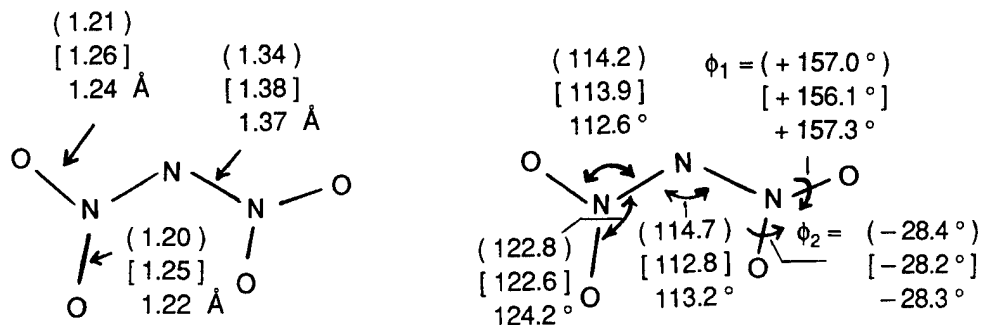[ ] - MP2/6-31+G(d)

no brackets - Experimental data[2] for ADN

(1.21)
[1.26]   (1.34)
   1.24 Å   [1.38]
                    1.37 Å

(114.2) ϕ_1 = (+ 157.0 °)
[113.9]   [+ 156.1 °]
   112.6 °   + 157.3 °

(122.8)   (114.7) ϕ_2 = (− 28.4 °)
[122.6]   [112.8]   [− 28.2 °]
   124.2 °   113.2 °   − 28.3 °

(1.20)
[1.25]
   1.22 Å

Figure 14

Calculated Bond Lengths and Angles of the Dinitramide Anion [N(NO$_2$)$_2^-$]

frequency (cm^{-1})	IR Intensity (cm^{-2}atm^{-1}@STP)	mode
719	48	N-N-N torsional bend
731	50	N-N-NO$_2$ rock
766	440	N-N-NO$_2$ rock
832	45	O-N-O bend

——— calculated [MP2/6-31+G(d)]

- - - - Cs$^+$N(NO$_2$)$_2^-$

Relative Intensity

600   800   1000
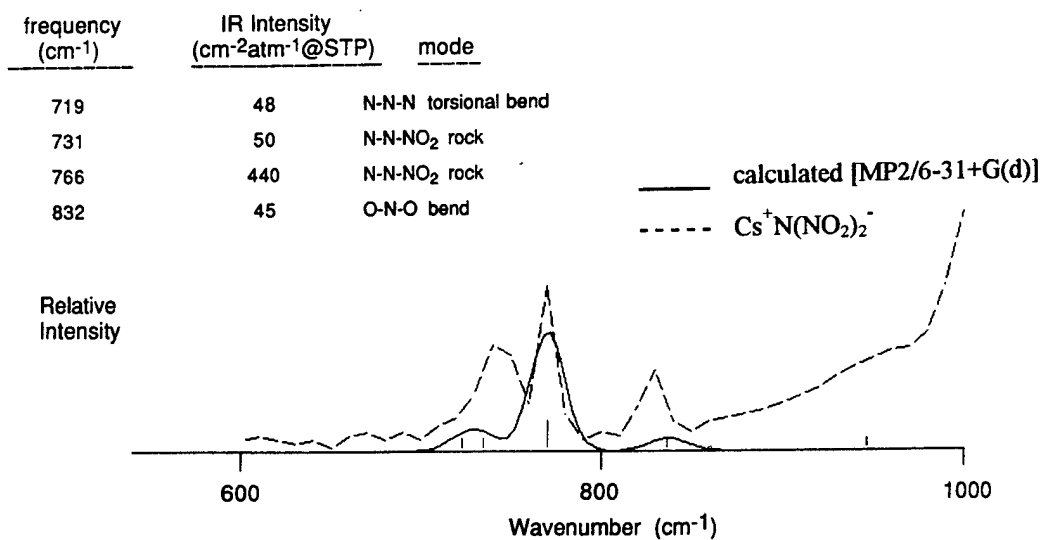
Wavenumber (cm^{-1})

Figure 15

Characteristic IR Features of the Dinitramide Anion [N(NO$_2$)$_2^-$]

28

3.4.2 ADN. The structure of ADN was analyzed at both the HF and MP2 correlated levels of theory. In Figure 16 the optimum structure for ADN at the RHF/6-31G(d, p) level is shown. This structure is very similar to that found by Gilardi[2] for the solid material and comprises a $NH_4^+N(NO_2)_2^-$ salt-like structure. A second stable form of ADN, as illustrated in Figure 17, is found at both the RHF and MP2 levels of theory. This structure, which probably represents the gas phase form of this material, consists of a weak NH_3-$N(NO_2)(NOOH)$ acid-base complex. The decomposition profiles observed by Fetheroff and Litzinger[3] and by Snelson[4] are consistent with decomposition of this acid-base complex to yield NH_3 and, through a concerted unimolecular decomposition of the $N(NO_2)_2$ group, to yield N_2O, H_2O, N_2 and NO_2. Thermodynamic calculations of ADN are incomplete, but preliminary calculations indicate $\Delta H_f(s)(298) = -36$ kcal/mol for ADN, in agreement with experimental data from China Lake.[5]
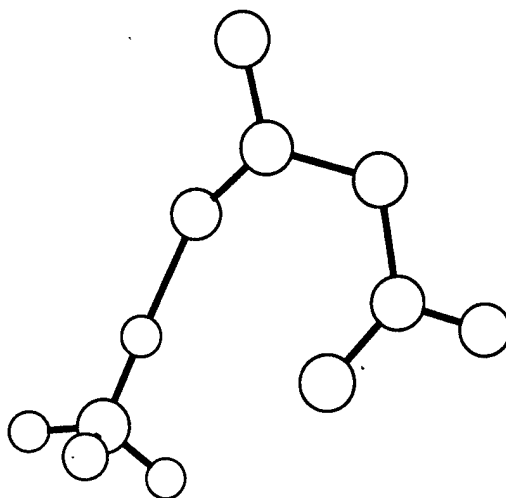

Figure 16

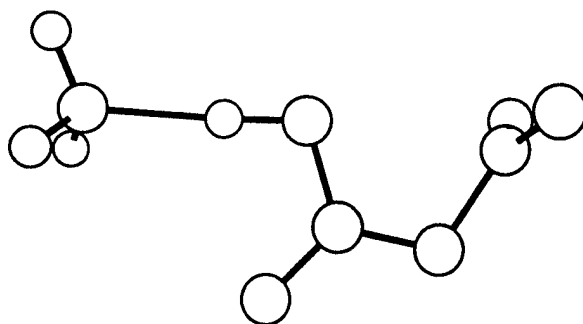**ADN [NH$_4$N(NO$_2$)$_2$] - C$_1$ Structure - RHF/6-31G(d, p) Level of Theory**

Figure 17

ADN [NH$_3$-HN(NO$_2$)$_2$ Complex] - C$_s$ Structure - MP2/6-31G(d) Level of Theory

[2] Gilardi: private communication, Naval Research Laboratory, 1992.

[3] Fetheroff, B. L. and Litzinger, T. A.: private communication, Pennsylvania State University, 1992.

[4] Snelson, A.: private communication, IIT Research Institute, 1993.

[5] Nadler: private communication, Naval Weapons Center, China Lake, CA, 1995.

3.4.3 HADN. The improved oxygen balance of hydroxyammonium nitrate (HAN) over ammonium nitrate suggested an examination of the stability of the parallel HADN structure. It was found that HADN is stable as a C_1 ionic structure with a calculated heat of formation of ~ -30 kcal/mol. Recent synthesis and characterization studies of this compound at SRI indicate that it is a liquid under normal conditions of temperature and pressure. Further studies of HADN were also carried out at the MP2 level of theory to more fully optimize the molecular structure. The results are illustrated in Figure 18, which suggests a salt-like structure, similar to that observed for ADN. Preliminary laboratory data from SRI suggest that HADN hydrolyzes readily and is probably only stable at low temperatures.
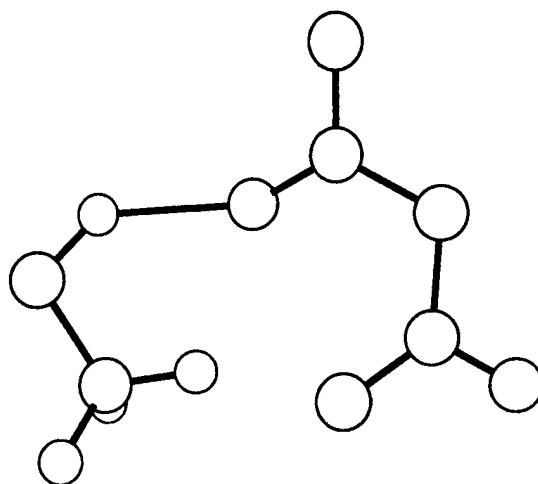
Figure 18

HADN [NH₃OH N(NO₂)₂] - C₁ Structure - RHF/6-31G(d, p) Level of Theory

3.4.4 Dinitraminic Acid. In the dinitramide series, of particular interest is the simplest compound, hydrogen dinitramide, which could exist as the smallest member of an organic alkyl-dinitramine series, $R-N(NO_2)_2$, or possibly as an inorganic acid of the form, $N(NO_2)(NOOH)$. Leroy, et al. (Refs. 28, 29) have reported gradient optimized RHF/4-31G and RHF/6-31G energies for $HN(NO_2)_2$ and have made semi-empirical estimates of its heat of formation, but they have not characterized the calculated molecular conformation or vibrational stability.

Ab initio calculations on $HN(NO_2)_2$ were performed at both the HF and MP2 levels of theory using the standard 6-31G(d, p), 6-31+G(d, p) and 6-311+G(d, p) basis sets. Although the calculated geometries are quite insensitive to the addition of diffuse basis functions, their use is necessary for thermochemical calculations involving the anion. Using the Gaussian system of programs (Ref. 15), gradient optimizations were performed to locate the geometries of the stationary points. Harmonic vibrational frequencies were then computed to verify that the calculated structures are true minima. The CADPAC electronic structure code (Ref. 30) was

used to perform the frequency analysis, since analytic second derivatives are available at the MP2 level of theory. Two stable conformations were located at both levels of theory. To assist in the analysis of the gas phase acidity of this molecule, parallel level of theory calculations were carried out for the dinitramide anion. This anion is found to be a C_2 structure at all levels of theory. The results are summarized in Appendix B-3, which contains an abstract of a technical paper on this system.

The minimum energy stationary point on the ground state surface corresponds to a C_s structure of the secondary amine form (nitro-form) [$HN(NO_2)_2$] of hydrogen dinitramide. A calculation of the 4-31G optimized geometry indicates that this is the structure found by Leroy, et al. (Refs. 28, 29). A second planar C_s structure is a metastable acid isomer. This acid-form [$N(NO_2)(NOOH)$] of hydrogen dinitramide is found to lie 9.4 kcal higher in energy than the nitro-form. Two other stable acid-forms are found which correspond to non-planar C_s structures arising from rotation of the nitro group. The chemistry of hydrogen dinitramide thus appears to be similar to that observed for nitromethane, [CH_3NO_2], where two tautomeric forms are known to exist (Ref. 31). Deprotonation of nitromethane occurs slowly in basic solution, and upon reacidification, the strongly acidic isomer is formed. In both compounds the acid-form reverts to the more stable nitro-form. The time constant for conversion between the two forms is dependent on the activation energy of the transition state above the acid-form. Apparently there is a sizable barrier for nitromethane, since the conversion occurs slowly at room temperature.

3.4.5 Trinitramine. Although there are many possible compounds of the form $RR'NNO_2$ and $RN(NO_2)_2$, there is only one possible trinitramine [$N(NO_2)_3$]. There has been speculation concerning the existence of trinitramine, but very few results have actually been reported to date.

Ab initio calculations were performed on pyramidal (C_3) and planar (D_{3h}) structures of $N(NO_2)_3$. Full geometry optimizations and harmonic vibrational frequency calculations were performed on both planar and pyramidal structures at the RHF/6-31G(d) level of theory. An additional MP2/6-31G(d) geometry optimization and harmonic vibrational frequency calculation was performed on the pyramidal structure. Thermochemical calculations include vibrational zero-point effects, estimated from the RHF/6-31G(d) vibrational frequencies scaled by 0.8929. A summary of the calculated results is given in Tables 17 and 18. The C_3 structure is shown in Figure 19.

Table 17. Calculated Energies and Geometries of Trinitramine [N(NO₂)₃]

Energies are in hartrees and geometries are in angstroms and degrees

Level of Theory	RHF/6-31G(d)		MP2/6-31G(d)		RHF/6-31G(d)	
Symmetry	C_3		C_3		D_{3h}	
Energy[a]	-66.44582	(0)	-668.26537	(0)	-66.40519	(3)
Geometry						
N-N	1.4444		1.5453		1.4663	
N-O₁	1.1713		1.2191		1.1698	
N-O₂	1.1757		1.2209		1.1698	
N-N-N	110.9		105.2		120.0	
N-N-O₁	112.6		111.0		116.2	
N-N-O₂	116.7		117.4		116.2	
N-N-N-O₁	-70.8		-76.0		0.0	
N-N-N-O₂	110.4		105.2		180.0	

[a] The number of imaginary vibrational frequencies is indicated in parenthesis.

Table 18. Calculated Vibrational Frequencies and IR Intensities of Trinitramine [N(NO₂)₃]

Level of Theory	RHF/6-31G(d)	MP2/6-31G(d)
Symmetry	C_3	C_3

Frequencies are in cm⁻¹ and IR intensities [ ] are in km/mol

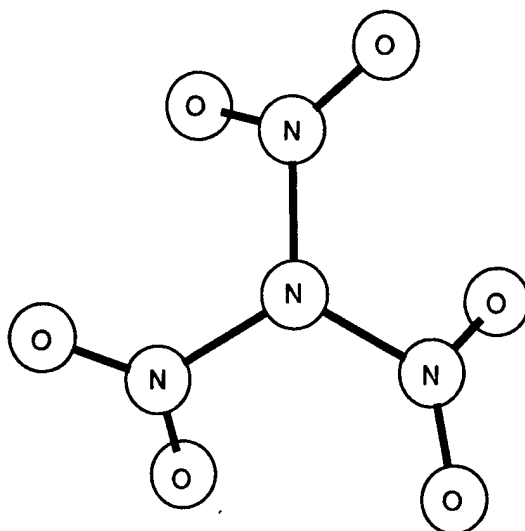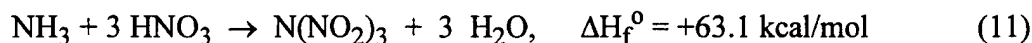| Group	A		E		A		E	
	127	[0.6]	53	[0.1]	96	[0.1]	43	[0.1]
	241	[5.0]	249	[3.7]	217	[2.1]	197	[4.2]
	444	[0.0]	508	[2.3]	325	[0.1]	321	[58.0]
	651	[4.7]	801	[8.7]	521	[0.2]	605	[59.7]
	937	[10.3]	908	[155.5]	796	[12.1]	748	[172.1]
	997	[9.3]	1155	[79.3]	835	[6.0]	800	[70.9]
	1641	[31.5]	1537	[290.8]	1350	[14.3]	1263	[180.6]
	1934	[869.1]	1979	[550.1]	1912	[90.5]	1921	[58.9]

Figure 19
Trinitramine Molecule [N(NO$_2$)$_3$] - C$_3$ Structure - MP2/6-31G(d) Level of Theory

As in ammonia, nitrogen trifluoride, and trimethylene, calculations show that trinitramine is pyramidal, not planar. At the RHF/6-31G(d) level, the planar structure is 24 kcal/mol higher in energy than the pyramidal ground state. The calculated vibrational frequencies for the pyramidal structure are all real, indicating this structure is a true minimum. Three of the RHF/6-31G(d) vibrational frequencies found for the planar trinitramine structure are imaginary, indicating that it is not a stable minimum or a transition state, and therefore no further calculations were performed on this structure.

The heat of formation of trinitramine, can be estimated from the heat of reaction for

$$NH_3 + 3\ HNO_3 \rightarrow N(NO_2)_3 + 3\ H_2O, \quad \Delta H_f^o = +63.1\ \text{kcal/mol} \quad (11)$$

or, alternatively, from

$$3\ NH_2NO_2 \rightarrow N(NO_2)_3 + 2\ NH_3, \quad \Delta H_f^o = +55.0\ \text{kcal/mol} \quad (12)$$

The MP2/6-31G(d) heats of formation calculated from the two reactions were averaged to obtain the final estimate, $\Delta H_f^o(N_4O_6) = +59.0$ kcal/mol. Analogous calculations (Ref. 20) of the heat of formation of nitric acid give an error of 1.7 kcal/mol. UTRC's estimated error in the calculated heat of formation of trinitramine is ±5 kcal/mol.

3.4.6 Nitrohydrazine Compounds. The nitration of hydrazine has been examined since the chemistry parallels that of the nitramides. Three vibrationally stable compounds are found from systematic nitration of hydrazine: 1,1-dinitrohydrazine [aminodinitramide], 1,2-dinitrohydrazine and tetranitrohydrazine [dinitramide dimer]. The first and last of these compounds are clearly in the dinitramide family. 1,2-dinitrohydrazine exhibits the highest stability in this group, with a central N-N bond length of 1.36 Å. All of these compounds are highly energetic and are suggested target molecules for synthesis activities. The structure of these molecules is illustrated in Figure 20 (see page 35). Tetranitrohydrazine $[(N(NO_2)_2)_2]$ with an estimated heat of formation of +128 kcal/mol and typical composite propellant density equal to that for AP, remains the main target compound for synthesis in this group.
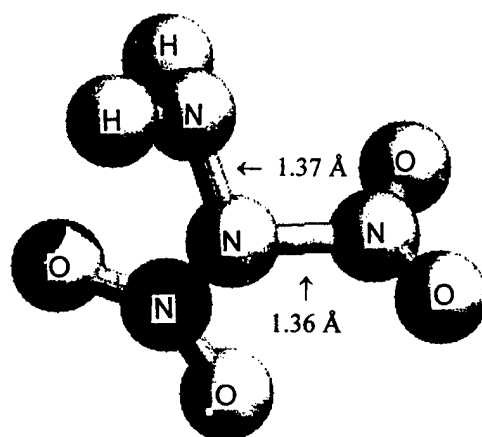
3.4.7 Dinitroborane. Studies were carried out on several nitroborane structures, including an extensive analysis of the simplest such compound, BH_2NO_2. Six structures of BH_2NO_2 have been theoretically characterized. The calculated results are summarized in Table 19 and Figure 21. Structures 1 and 2 have been previously studied (Ref. 32), while Structures 3-6 are new.

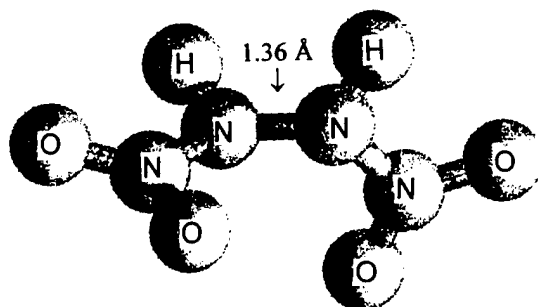**Table 19. Calculated Results for BH_2NO_2 Structures**

Structure	RHF/6-31G(d)	MP2/6-31G(d)
1	-229.87736 [1]	-230.49038 [1]
2	-229.88688 [0]	-230.49858 [1]
3	---	-230.50913 [0]
4	-229.92361 [1]	-230.53460 [0]
5	-229.93967 [0]	-230.53965 [0]
6	-229.93285 [1]	-230.53598 [0]

The number of imaginary vibrational frequencies is given in parenthesis following the calculated energy. No RHF stationary point was found for Structure 3.
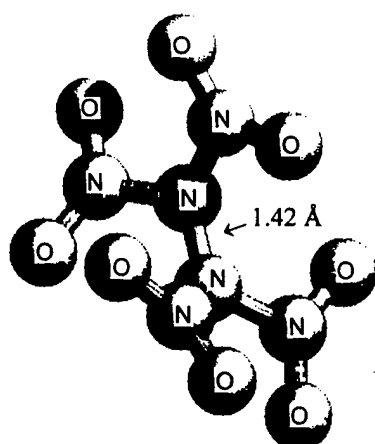
From Figure 21, Structures 1-3 can be seen to have a nitro-form, and Structures 4-6 are nitrite compounds. Electron correlation plays a very significant role in determining the vibrational stability of the various BH_2NO_2 structures, as three of the six reported structures change from minima to saddles, or vice versa, when the level of theory is taken from RHF/6-31G(d) to MP2/6-31G(d). This is a peculiarity of nitroboranes, because of their electron deficient nature. Also a consequence of the electron deficiency is the tendency to form bridged Structures (3-4) and to prefer the formation of B-O bonds. Thus, the stable structures are somewhat different than those found for nitromethane and nitramide.

1,1-dinitrohydrazine [aminodinitramide]
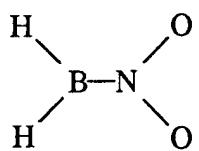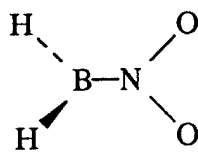[^{1}A] - C$_1$ Symmetry

1,2-dinitrohydrazine
[^{1}A] - C$_2$ Symmetry
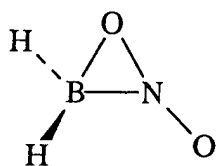

Tetranitrohydrazine
[^{1}A] - C$_2$ Symmetry

Figure 20
Nitrohydrazine Compounds
35

1

2

3

4

5

6

Figure 21
BH_2NO_2 Structures

36

Heats of formation can be estimated from the reaction

$$BH_3 + HNO_3 \rightarrow H_2O + BH_2NO_2 \qquad (13)$$

using the calculated MP2/6-31G(d) heat of reaction and the known heats of formation of borane, nitric acid, and water. The heat of formation of Structure 3 is estimated to be -4 ±5 kcal/mol and that of Structure 5 is estimated to be -16 ±5 kcal/mol.

A transition state for the interconversion of Structures 3 and 4 has been located and gives a barrier > 100 kcal/mol for this process. Therefore, it may be that both nitro and nitrite forms of BH_2NO_2 exist as stable species. The interconversion of Structures 4-6 is undoubtedly more facile.

Further studies at higher levels of theory will be necessary to determine conclusively the energetics and stability of BH_2NO_2. However, it appears from the present calculations that there are no direct boron analogues of nitromethane and nitramide, and this suggests that boron analogues of dinitramide will probably be bridged or other such unconventional structures. This speculation is confirmed by detailed calculations on dinitroborane structures. The $HB(NO_2)_2$ analogue of HDN is found to be a saddle point at the MP2/6-31G(d) level of theory, but a bridged C_1 structure, analogous to BH_2NO_2, Structure 3, is found to be a stable minimum. This structure is shown in Figure 22. Additionally, a C_{2v} ring structure, shown in Figure 23, has been found to be stable at the MP2/6-31G(d) level, and lies about 60 kcal/mol higher in energy than the structure of Figure 22.

Further work is needed to characterize these structures, and assess their potential as high energy density matter (HEDM) compounds.
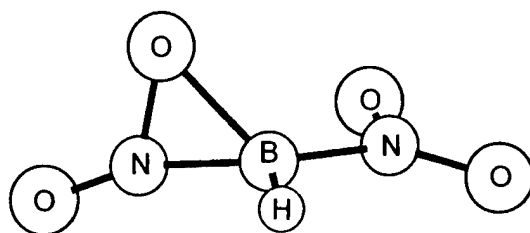

Figure 22
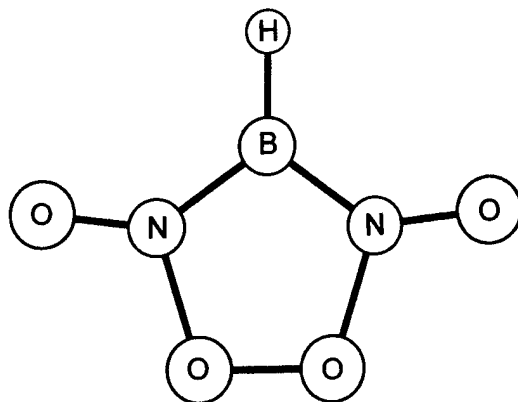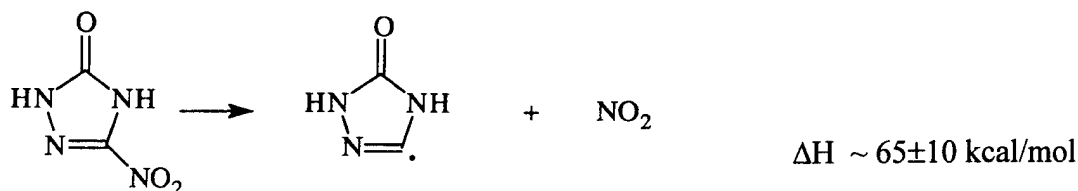**[HB(NO₂)₂] - C₁ Structure**

Figure 23
[HB(NO$_2$)$_2$] - C$_{2v}$ Structure
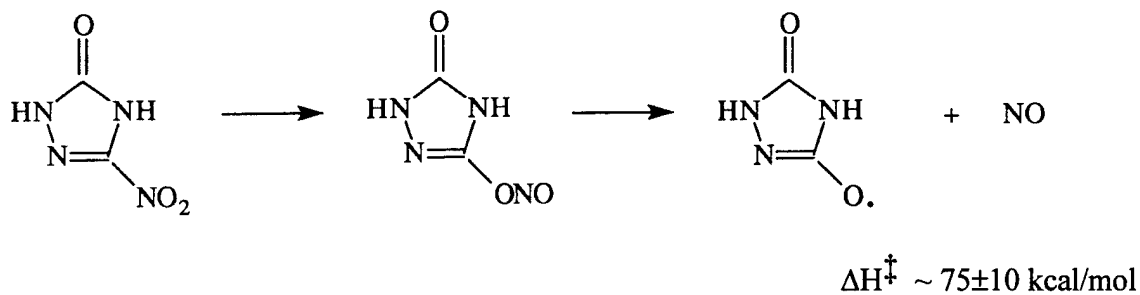
3.5 Nitrated Ring Structures

3.5.1 NTO. A study was initiated on substituted triazole and tetrazole compounds that may exhibit high energy content with less sensitivity to shock than nitrated cyclic compounds such as RDX and HMX. The development of explosives with lessened sensitivity to detonation by shock or impact is an area of considerable current interest. There are several factors which, when taken together, determine the impact or shock sensitivity of an energetic material. At one end of the scale is the interaction of the bulk material (crystal or polymer) with the applied external force, leading to deformation, compression, and ultimately, the localization of energy, creating "hot spots". At the other end of the scale is the molecular thermochemistry of the energetic material, as measured by bond dissociation energies and barrier heights for rearrangement and decomposition. These determine the molecular pathways for assimilation of energy applied externally to the bulk material. Full understanding of the nature of shock sensitivity in energetic materials requires investigation of both bulk and molecular phenomena.

In particular, 3-nitro-1,2,4-triazol-5-one (NTO) is now being considered for use as an insensitive explosive. Partly based on semiempirical (PM3) calculations, preliminary estimates have been made of the thermochemistry of the thermal decomposition of NTO. The possible pathways that have been examined are:

1) C-NO$_2$ bond breaking

$\Delta H \sim 65 \pm 10$ kcal/mol

38

2) NO$_2$ → ONO rearrangement and subsequent bond breaking

$$\Delta H^{\ddagger} \sim 75\pm10 \text{ kcal/mol}$$

3) N-H bond breaking

$$\Delta H \sim 78\pm10 \text{ kcal/mol}$$

4) concerted unimolecular decomposition

NH + HNCO + NCNO$_2$

$$\Delta H^{\ddagger} \sim 100\pm10 \text{ kcal/mol}$$

5) nitronic acid formation

$$\Delta H^{\ddagger} > 100 \text{ kcal/mol}$$

UTRC's estimate of 65 kcal/mol for the C-NO$_2$ bond is about 20-30 kcal/mol above current estimates of the N-NO$_2$ bond strength in materials such as RDX and provides, in combination

39

with thermochemical estimates for Alternatives 2 through 5, a simple molecular explanation of the lessened sensitivity of NTO relative to RDX and HMX.

Although the lowest energy pathway suggested by preliminary calculations is via Alternative 1 (C-NO$_2$ bond breaking), Alternatives 2 and 3 are energetically close enough that more accurate calculations might reverse their order. Indeed, there is evidence that NTO/acetone solutions decompose via solvent-assisted hydrogen abstraction, and it is possible that N-H bond breaking could be the lowest energy decomposition channel. It is clear that a more detailed study of the molecular thermochemistry of NTO and similar materials is necessary to understand their thermal decomposition pathways.

3.5.2 Nitrozoles. Studies were initiated on the structure and stability of several substituted triazoles and tetrazoles based on discussions with the SRI synthesis group. The baseline compound for comparison is NTO, which is a shock-insensitive explosive. NTO is described in detail in the previous section. There is a stable structure with C$_s$ symmetry for 1-amino-3-nitro-1,2,4-triazole (ANT); 1-amino-3,5-dinitro-1,2,4-triazole (ADNT); and a planar structure with C$_s$ symmetry for 1-fluoro-3-nitro-1,2,4-triazole. All of these compounds are highly energetic relative to NTO.

Higher energy structures can be synthesized by further nitrogen substitution in the ring. For example, there is stability for 1-amino-3-nitrotetrazole in C$_s$ symmetry. This compound has a very high heat of formation (+96.5 kcal/mol) and has recently been synthesized at SRI.

The calculated structures for this class of energetic compounds are illustrated in Figures 24 through 28. The calculated solid densities and estimated gas phase heats of formation are shown in Table 20.

Figure 24

[NTO] 3-nitro-1,2,4-triazole-5-one (C$_2$H$_2$N$_4$O$_3$) - C$_s$ Symmetry, ^{1}A'
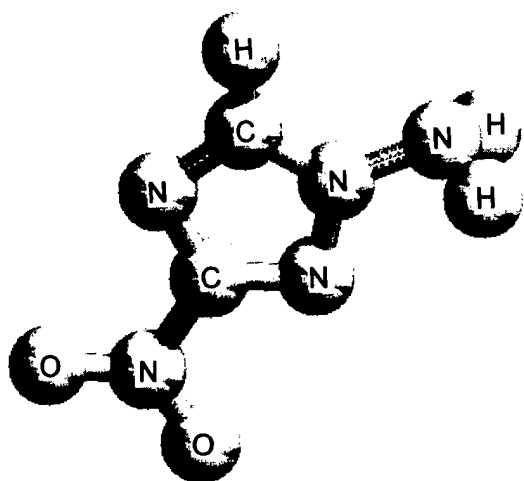
Figure 25

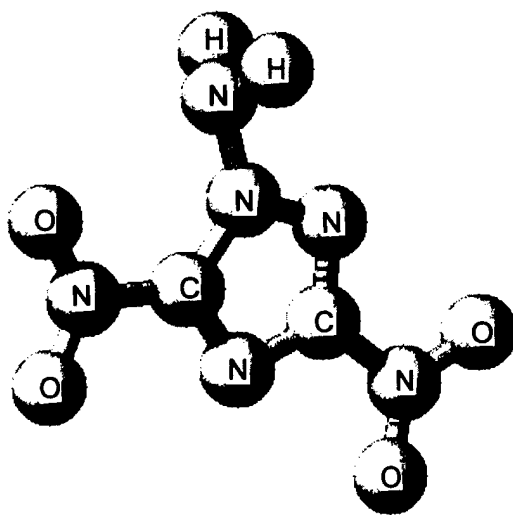[ANT] 1-amino-3-nitro-1,2,4-triazole $(C_2H_3N_5O_2)$ - C_s Symmetry, $^1A'$

Figure 26

[ADNT] 1-amino-3,5-dinitro-1,2,4-triazole $(C_2H_2N_6O_4)$ - C_s Symmetry, $^1A'$
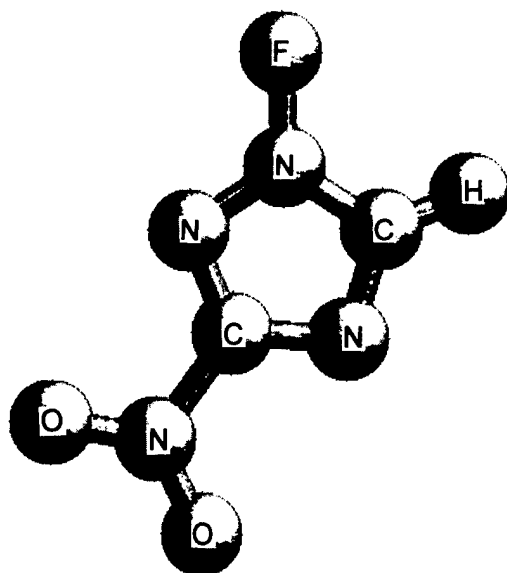
Figure 27

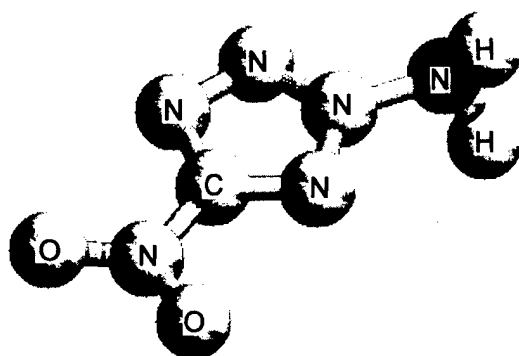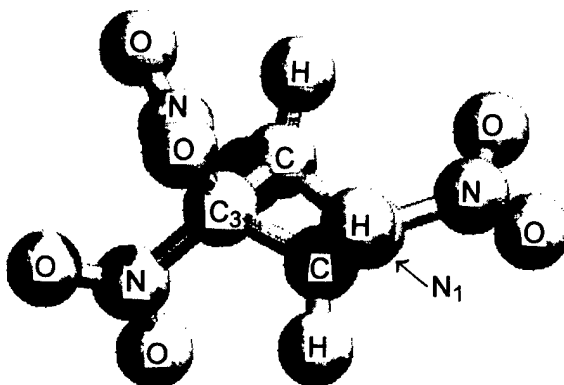[FNT] 1-fluoro-3-nitro-1,2,4-triazole $(C_2HFN_4O_2)$ - C_s Symmetry, $^1A'$

Figure 28

1-amino-3-nitrotetrazole $(CH_2N_6O_2)$ - C_s Symmetry, $^1A'$

Table 20. Thermochemistry of Advanced Propellants

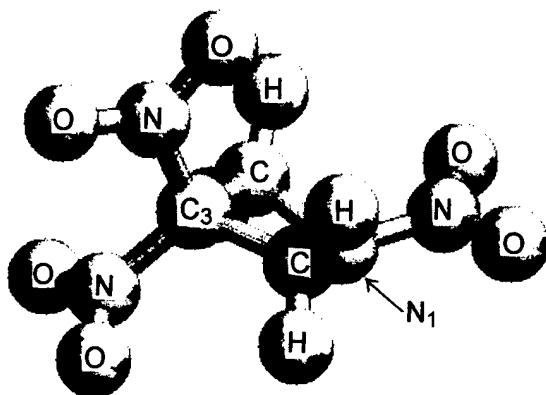| Compound	Formula	Mol. Wt.	Density gm/cm^3	$\Delta H_f(25°C)$ kcal/mol
			1.80	-36.0
ammonium dinitramide [ADN]	$H_4N_4O_4$	124.056	1.75	+8.3 (g)
nitrosyldinitramide	N_4O_5	136.023	1.94	+49.8
trinitramine	N_4O_6	152.022	2.15	+80.4
1,1-dinitrohydrazine (aminodinitramide)	$H_2N_4O_4$	122.040	2.04	+58.6
1,2-dinitrohydrazine	$H_2N_4O_4$	122.040	2.04	+44.3
tetranitrohydrazine	N_6O_8	212.034	2.17	+128.2
bis [nitroamino] nitrosylamine anion	$N_5O_5^-$	150.030	1.92	+57.9
diazidamine	H_1N_7	99.057	1.56	+199.0
triazidamine	N_{10}	140.070	1.58	+302.0
diazidonitronium cation	N_7O^+	114.048	1.65	+397.1
nitrosylazide	N_4O	72.027	1.54	+115.4
nitrylazide	N_4O_2	88.026	1.76	+95.1
3-nitro-1,2,4-triazol-5-one [NTO]	$C_2H_2N_4O_3$	130.063	1.75	-10.5
1-amino-3-nitro-1,2,4-triazole [ANT]	$C_2H_3N_5O_2$	129.079	1.61	+55.6
			[1.70]	[+50.0] (exp.)
1-amino-3,5-dinitro-1,2,4-triazole [ADNT]	$C_2H_2N_6O_4$	174.076	1.77	+73.2
5-amino-2,4-dinitro-1,3,5-triaza-bicyclo[2,1,0]pent-2-ene	$C_2H_2N_6O_4$	174.076	1.92	+173.3
1-fluoro-3-nitro-1,2,4-triazole [FNT]	$C_2HFN_4O_2$	132.054	1.68	+76.2
1-amino-3-nitrotetrazole	$CH_2N_6O_2$	130.067	1.67	+96.5
dioxopentazolide anion	$N_5O_2^-$	102.033	1.76	+100.4
nitroacetylene	C_2HNO_2	71.035	1.51	+71.7
dinitroacetylene	$C_2N_2O_4$	116.032	1.79	+94.8
1-nitropropylene	$C_3H_3NO_2$	85.062	1.37	+57.8
nitrylcyanide	CN_2O_2	72.023	1.82	+58.0
1,3,5-trinitro-1,3,5-triazacyclohexane [RDX]	$C_3H_6N_6O_6$	222.117	1.76	+53.5
1,3-dinitro-1,3-diazacyclobutane [HEDMX]	$C_2H_4N_4O_4$	148.078	1.76	+53.7
1,3,3-trinitroazididine [TNAZ]	$C_3H_4N_4O_6$	192.087	1.78	+35.0

3.5.3 Nitramines/Azididines. Cyclic nitramines that also contain geminal dinitroalkyl groups have recently been synthesized (Refs. 33-36). These compounds may exhibit an increase in oxygen balance over the corresponding compounds with mononitroalkyl groups. A compound of primary interest in this group is TNAZ, a four-membered ring in the RDX, HMX series that exhibits a single dinitroalkyl group. Other compounds in this series include 1,3,5,5-tetranitrohexahydropyrimidine [DNNC] and 1,3,3,5,7,7-hexanitro-1,5-diazacyclooctane [HNDC], which are analogues of RDX and HMX, respectively.

An extensive set of *ab initio* calculations has been carried out on TNAZ. Eight possible conformations of TNAZ were examined at the HF/3-21G and HF/6-31G(d) levels of theory. The ground state conformation has the nitro groups at ring Positions 1 and 3 in a perpendicular trans-arrangement, relative to the azididine ring. A second very low-lying conformation (+0.3 kcal) has the nitro groups at ring Positions 1 and 3 in a perpendicular cis-arrangement to the azididine ring. There appears to be nearly free rotation of the nitro-groups at ring Position 3. A transition state energy is calculated at +2.0 kcal when both nitro groups at Position 3 are perpendicular to the azididine ring. Figures 29 and 30, respectively, show these low-lying cis- and trans-conformations of azididine. If similar results are found at a correlated level of theory, there may be more than one polymorph of this compound.

(nitro groups at ring Positions 1 and 3 are cis to ring)

Figure 29
1,3,3-trinitroazididine (cis) - C_s Symmetry, $^1A'$

44

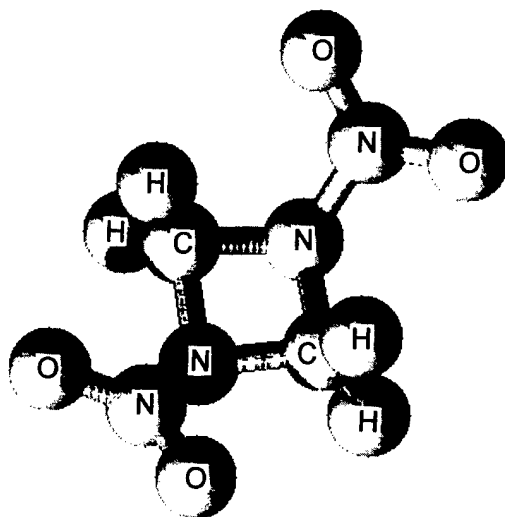(nitro groups at ring Positions 1 and 3 are trans to ring)

Figure 30
1,3,3-trinitroazididine (trans) - C_s Symmetry, $^1A'$

Correlated calculations of the ground state of TNAZ were next attempted. This system, however, proved to be too extensive for current computer capabilities. Instead, based on a fully optimized C_s structure (25 geometric parameters), the heat of formation of this molecule was calculated using the method outlined by Ibrahim and Schleyer (Ref. 37). A value of ΔH_f^O (25°C) = + 35.0 kcal/mol was obtained for the gas phase heat of formation. Estimated corrections for the sublimation energy indicate that TNAZ is more energetic than NTO but less energetic than the recently synthesized 1-amino-3-nitro-1,2,4 triazole compound.[6] UTRC's calculated density for TNAZ is 1.78 g/cc (Cady's method), slightly greater than that for NTO (1.75 g/cc).

In addition to studies of TNAZ, an evaluation of cyclodimethylenedinitramine (1,3-dinitro-1,3-diazacyclobutane) was undertaken. This compound is the smallest ring member in the RDX, HMX nitramine series. There is a stable structure with C_s symmetry as illustrated in Figure 31. The estimated heat of formation of this new compound is +54 kcal/mol, indicating that, on a mass basis, this is a much more energetic structure than either RDX or HMX. The calculated solid density is 1.76 g/cc (Cady's method), a value somewhat smaller than that for RDX (1.80 g/cc).

Correlated calculations of cyclodimethylenedinitramine were undertaken for this smallest ring member in the RDX, HMX nitramine series. A stable C_{2v} structure with $^1A_1$ symmetry is found at the MP2/6-31G(d) level of theory. The lowest frequency mode [a_1 = 64 cm^{-1}] is a symmetric axial stretch of the C-N-C-N ring, indicating that this compound may have lower ring strain energy than expected, offering some chance for ring closure in synthesis attempts. The name HEDMX is suggested as an identifier for this new cyclic nitramine.

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[6] Schmitt,R.: private communication, SRI International, 1995.

(smallest member of RDX, HMX nitramine series)

Figure 31
1,3-dinitro-1,3-diazacyclobutane - C_{2v} Symmetry, $^1A_1$

3.6 Substituted Prismanes

Ab initio calculations were performed to determine the structure and stability of [3]-prismane and its nitro derivatives. (The simplifying notation of prismane is adopted for the smallest member of the [n]- prismane group of compounds.) In Figure 32, the stable D_{3h} structure of unsubstituted prismane is illustrated. Next the prismane carboxylic acid structure

Figure 32
Prismane [C_6H_6] as a D_{3h} Structure

was examined, since such substituted compounds are known for [4]-prismane (cubane) and may provide a synthesis entry point for other functional groups. A stable dicarboxylic acid structure of prismane has been found that exhibits C_2 symmetry, as illustrated in Figure 33. In addition, stable forms of both nitroprismane and dinitroprismane were found, as illustrated in Figures 34 and 35, respectively.

Figure 33

Prismane Dicarboxylic Acid [$C_6H_4(COOH)_2$] - C_2 Structure

Figure 34

Nitroprismane [$C_6H_5NO_2$] - C_s Structure

Figure 35

Dinitroprismane [C₆H₄(NO₂)₂] - C₂ Structure

A preliminary evaluation of the thermochemistry of prismane and substituted prismane has been carried out. Gradient optimized structures for prismane, nitrotriprismane, and dinitroprismane were obtained at the RHF/6-31G(d) level of theory. Calculations of the harmonic vibrational frequencies demonstrated these to be vibrationally stable structures. Following Schulman and Disch (Ref. 38), the homodesmic reactions

$$6 \text{ isobutane} \rightarrow \text{prismane} + 9 \text{ ethane} \tag{14}$$

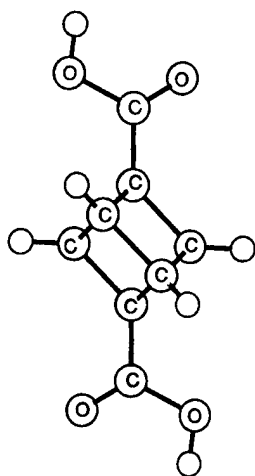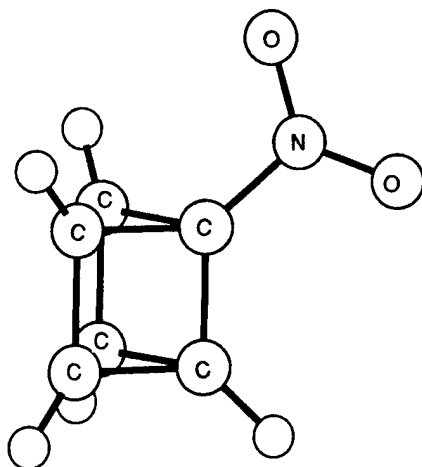$$5 \text{ isobutane} + \text{nitrobutane} \rightarrow \text{nitroprismane} + 9 \text{ ethane} \tag{15}$$

$$4 \text{ isobutane} + 2 \text{ nitrobutane} \rightarrow \text{dinitroprismane} + 9 \text{ ethane} \tag{16}$$
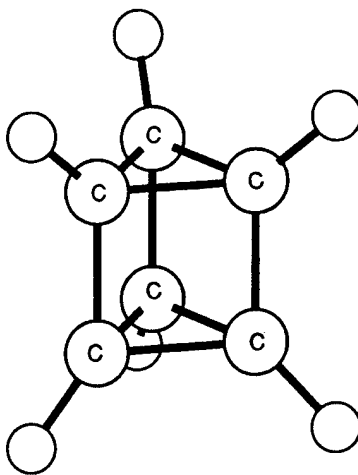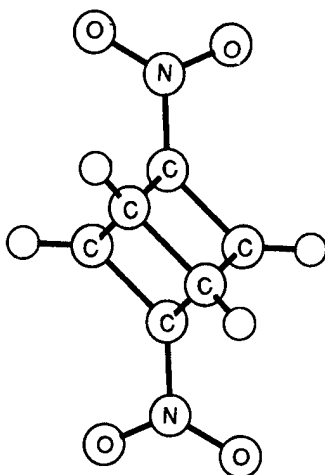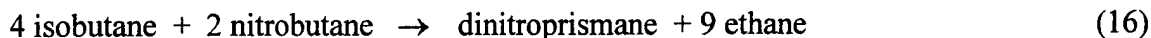
were used to calculate the heat of formation of these structures. The enthalpy change in these reactions provides a theoretical estimate of the strain energy (Ref. 39). These calculations suggest that nitroprismane and dinitroprismane are not significantly more strained than prismane. The calculated heats of formation and strain energies are shown in Table 21.

Table 21. Calculated Heats of Formation and Strain Energy of Prismanes
MP2/6-31G(d, p) Level of Theory

	Heat of Formation (kcal/mol)	Strain Energy (kcal/mol)
Prismane	+ 135	+147
Nitroprismane	+ 125	+150
Dinitroprismane	+ 122	+159

Several synthesis routes for the nitroprismanes are being evaluated at United Technologies Chemical Systems Division. A five-step synthesis route to the dicarboxylic acid structure shown in Figure 33 has been formulated. Formation of the nitro-forms from the dicarboxylic acid structure may follow along routes similar to those known to yield nitrocubanes starting from the carboxylic acid form of cubane.

4.0 CONCLUSIONS AND RECOMMENDATIONS

The main objective of this research program was to identify those light element molecular species that have sufficient internal energy to be useful in advanced chemical propulsion systems. Other objectives were to characterize the available energy content of these new compounds, to investigate probable kinetic routes for their formation and decomposition, to characterize vibrational spectra and other molecular properties and to suggest possible synthesis routes. The utility of these new compounds in chemical propulsion systems was analyzed through calculations of specific impulse of propellant formulations that incorporated these materials.

In a previous study (Ref. 40) the focus was on light element, high symmetry structures such as Li_3H, azide-like structures such as a-N_2O_2 and FN_3, and hypervalent structures such as NF_5. During the course of the current program, the emphasis shifted to studies of advanced oxidizers, including characterization of the new family of dinitramide compounds. Toward the end of this contract, as computational tools improved, it was possible to study some very complicated energetic ring structures. The compounds that were studied can be categorized into six groups:

1. high symmetry hypervalent structures [OF_6]
2. azide-like structures [$N(N_3)_3$, $HN(N_3)_2$, $N(N3)_2^-$, $N(N_3)_4^+$, NON_3, NO_2N_3, $B_2H_2(N_3)_4$, $HB(N_3)_2$, $HNBN_3$]
3. nitrated cyclic and polycyclic nitramine compounds [RDX, HMX, CL20, PCNs]
4. dinitramide compounds [$N(NO_2)_2^-$, LiDN, ADN, HADN, $HN(NO_2)_2$, $N(NO_2)_3$, $N(NO_2)_4^+$, $H_2NN(NO_2)_2$, $(HNNO_2)_2$, $(N(NO_2)_2)_2$, BH_2NO_2, $B(NO_2)_2^-$, $HB(NO_2)_2$]
5. nitrated ring compounds [NTO, TNAZ, ANT, ADNT, FNT, HEDMX]
6. substituted prismanes [triprismane, nitrotriprismane, dinitrotriprismane, triprismane carboxylic acid]

A summary of the results and recommendations for further research into these several groups of compounds follows.

4.1 High Symmetry Hypervalent Structures

Studies of OF_6 indicate that this high symmetry structure may exist as a gas phase species exhibiting mainly covalent bonding. However, there is a low transition state barrier for formation of the ionic $F^-OF_5^+$ structure which has low energy content. The chemistry of this compound thus resembles that for NF_5. It may be of interest to study OF_4 and other mixed oxidizers, but the potential for significant I_{sp} improvement from the class of oxidizers appears to be limited.

4.2 Azide-like Structures

All of the new azide-like structures that were examined exhibit very large positive heats of formation. The chemistry of the diazidamide anion parallels that for the dinitramide anion but exhibits much higher energy content. The fundamental problem with azidamines is their low energy barrier for nitrogen elimination. This characteristic was observed experimentally in the work by Benard at Rockwell Science Center (Ref. 41), where TADB dissociated upon heating to yield B-N structures with much lower energy content. Nitrosyl azide and nitryl azide are known energetic compounds but require very low temperature synthesis and exhibit no long-term stability. This class of compounds (azides) is chemically interesting and highly energetic, but it exhibits limited structural stability, even offering explosive character. Further research in this area is warranted, however, since synthesis techniques for azide-like structures are often applicable to other classes of compounds that exhibit low decomposition barriers.

4.3 Nitrated Cyclic and Polycyclic Compounds

Nitramine chemistry is presently a dynamic area for synthesis of new compounds. Although compounds such as RDX and HMX have been known for decades, there was little new activity until the 1980s when interest was renewed in nitramines based on the development of caged polycyclic structures. These new compounds, such as adamantane and wurtzitane, are synthesized by forming C-C bridges between the rings of two or more alcane structures. The successful, and amazingly simple, synthesis of CL20 constituted a major advance in synthesizing nitramines with much higher energy content. Calculations of CL20 confirm the structure of this molecule and verify the high positive heat of formation. Based on studies of CL20, several new polycyclic nitramine structures were analyzed. The first compound: 3,5,8,10,11,12-hexanitro-3,5,8,10,11,12-hexaazatetracyclo ☐ ($5.3.1.1.^{2,6}0^{4,9}$) dodecane, is formed by carbon-bridging on two RDX molecules. This compound exhibits vibrational stability in C_s symmetry but has a negative oxygen balance. A second compound of this type can be formed by carbon-bridging on two HMX molecules. This compound: 3,5,7,10,12,14,15,16-octanitro-3,5,7,10,12,14,15,16-octaazapentacyclo ☐ ($7.5.1.1^{3,8}0.^{4,13}0.6,11$) heaxadecane, also exhibits vibrational stability in C_s symmetry but still has an oxygen balance of -4 O atoms. Next, nitrogen-bridging on two RDX molecules was examined and a stable pentadecane structure was found: 2,4,6,8,10,12,13,14,15-

nonanitra-2,4,6,8,10,12,13,14,15-nonaazatetracyclo □ $(5.5.1.1^{3,11}1^{5,9})$ pentadecane. This is the first polycyclic nitramine that has been analyzed that exhibits a positive oxygen balance (+3 O atoms). Synthesis activities on these new polycyclic nitramines appears to be warranted.

4.4 Dinitramide Compounds

As is now well known, the chemistry of dinitramide compounds was developed independently in both Russia (Ref. 27) and by Bottaro and Schmitt[1] at SRI. Several new compounds, mainly alkali and ammonium salts, were synthesized that exhibit the basic $N(NO_2)_2^-$ structure. UTRC undertook an extensive study of this new inorganic anion and several new dinitramide compounds. Calculations confirmed the x-ray structure of the dinitramide anion and shed light on decomposition pathways. Several new compounds were examined for structural stability, including $N(NO_2)_3$ and HADN. Both of these compounds were later synthesized by SRI but exhibit limited stability, except at low temperatures [$N(NO_2)_3$], or appear to hydrolyze readily to a liquid [HADN]. Extensive propellant formulation activities are currently in progress with the parent compound of this group [ADN], since it is a proposed chlorine-free replacement for AP.

This dinitramide group can also be realized by systematic nitration of a starting compound such as hydrazine. There are three vibrationally stable compounds: 1,1-dinitrohydrazine, 1,2-dinitrohydrazine and tetranitrohydrazine. The first and last compound in this group exhibit a dinitramide structure; 1,1-dinitrohydrazine (aminodinitramide) exhibits the -NH_2 group, suggesting that the activating effect of this primary amine group could lead to a high degree of reactivity. The jewel in this group appears to be tetranitrohydrazine, which exhibits very little central N-N bond stretching upon complete nitration of the parent hydrazine molecule. A performance of I_{sp} = 300 sec is predicted using this oxidizer with R45M as a binder. On a density impulse basis, nearly 15% improvement in performance can be realized. This compound should be a leading candidate for synthesis activities of advanced oxidizers.

The chemistry of the nitroborane [$B(NO_2)_2^-$] structures that parallel dinitramide structures is not fully understood. Both the nitro and nitrite forms of BH_2NO_2 are conformationally stable, but there appear to be no stable boron analogues of nitromethane or dinitramide. Preliminary studies indicate that B-bridged structures are formed but, clearly, more studies are indicated for this chemistry area.

4.5 Nitrated Ring Structures

Following discussions with several groups working on the development of explosives with lessened sensitivity to detonation, UTRC undertook calculations on several substituted triazole and tetrazole compounds. The baseline compound that was examined was NTO which is a prototype as an insensitive explosive. Calculations indicated a planar structure for this compound with a calculated heat of formation of -10 kcal/mol. These results are in excellent agreement with the known experimental characteristics of this compound and suggest that this

level of theory was adequate for an initial evaluation of stability and energy content. The several possible decomposition pathways for NTO were examined, which indicated that $C-NO_2$ bond breaking is the lowest energy decomposition pathway. Further studies of the decomposition pathways for NTO are currently in progress by K. Lammertsma[7] at the University of Alabama.

Studies were then focused on the structure, stability and energy content of TNAZ. There are two stable conformations for this compound lying only 0.3 kcal/mol apart. Further, there are very low barriers for nitro-group rotation in this system, leading to a complicated spectra. The calculated heat of formation for TNAZ is +35.0 kcal/mol., a value much higher than for NTO. This compound should be further studied, including an accurate analysis of its thermochemistry.

Beyond TNAZ, calculations were undertaken on several compounds that were suggested or already synthesized by SRI. They include 1-amino-3-nitro-1,2,4-triazole; 1-amino-3,5-dinitro-1,2,4-triazole; 1-fluoro-3-nitro-1,2,4-triazole; and 1-amino-3-nitrotetrazole. This last compound has a heat of formation similar to CL20 [+96.5 kcal/mol] and exhibits reasonable stability. The triazoles that were examined exhibit +50 to +70 kcal/mol for calculated heats of formation.

Finally, 1,3-dinitro-1,3-diazacyclobutane, the smallest member in the RDX, HMX nitramine series, was examined. Studies of TNAZ suggested that this compound should exhibit stability. This compound has a molar heat of formation similar to RDX and surprisingly little strain energy in the ring. HEDMX is suggested as an identifier for this new cyclic nitramine, which is a prime target for experimental synthesis.

4.6 Substituted Prismanes

The last series of compound, [n]-prismanes, was not completely evaluated. Experimental activities at Phillips Laboratory and other centers indicate that this class of compounds may be useful in improving the I_{sp} in the propellant fuel/liquid oxygen (LP-1/LOX) propulsion systems. Cubane addition to LP-1 has already been demonstrated to yield an improvement in I_{sp}. Calculations indicate that both the nitroprismanes and dinitroprismane structures are stable. Nitration lowers the heat of formation by ~ 10% but these compounds exhibit high heats of formation (+100 to +125 kcal/mol) in any case, owing to their high strain energy. Further synthesis and compound characterization activities should be encouraged for this class of strained hydrocarbons.

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[7] Lammertsma, K.: private communication, University of Alabama, 1994.

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APPENDIX A

PUBLICATIONS AND PRESENTATIONS

The significant research results obtained under this contract have been prepared for publication in technical journals or presented at technical meetings. These papers and meetings are listed below. Abstracts of the published papers are included in Appendix B. All of these papers can be found in the open literature.

A. Technical Reports in Journals and Books

1. "Investigation of Two Potential Visible Wavelength Chemical Laser Schemes Based on Thermal Dissociation of Chlorine Azide". D. J. Benard, B. K. Winker, M. A. Chowdhury, T. A. Seder and H. H. Michels, Proceedings of the international Conference on Lasers '91, edited by F. J. Duarte and D. G. Harris, STD Press, McLean, Virginia, 1991, pp.188-203.

2. "Theoretical Studies of Spin Forbidden Radiationless Decay in Polyatomic Systems. II: Radiationless Decay of a-N_2O_2". K. A. Nguyen, M. S. Gordon, D. F. Yarkony, J. A. Montgomery, Jr. and H. H. Michels, *Journal of Chemical Physics*, **98**, 1993, pp. 3845-3849.

3. "On the Structure and Thermochemistry of Hydrogen Dinitramide". H. H. Michels and J. A. Montgomery, Jr., *Journal of Physical Chemistry*, **97**, 1993, pp. 6602-6606.

4. "Structure and Stability of Trinitramide". J. A. Montgomery, Jr. and H. H. Michels, *Journal of Physical Chemistry*, **97**, 1993, pp. 6774-6775.

5. "Energy Transfer from Metastable NF to Boron Hydride". D. J. Benard, E. Boehmer, H. H. Michels and J. A. Montgomery, Jr., *The Journal of Physical Chemistry*, **98**, 1994, pp. 8952-8958.

6. "Structures, Bonding and Energetics of N_2O_2 Isomers". K. A. Nguyen and M. S. Gordon, J. A. Montgomery, Jr., and H. H. Michels, *The Journal of Physical Chemistry*, **98**, 1994, pp. 10072-10078.

7. "Theoretical Prediction of the Structures and Stabilities of Azidamines". H. H. Michels, J. A. Montgomery, Jr., K. O. Christe and D. A. Dixon, *Journal of Physical Chemistry*, **99**, 1995, pp. 187-194.

8. High Specific Enthalpies from the Photochemically Induced Isomerization: BOH ↔ HBO". J. L. Gole and H. H. Michels, *Journal of Chemical Physics*, **103**, 1995, pp.7844-7850.

B. Presentations

1. "Electronic Structure and Thermochemical Properties of Advanced Oxidizers". H. H. Michels and J. A. Montgomery, Jr., 5th HEDM Contractors' Conference, Albuquerque, New Mexico, February 24 - 27, 1991, PL-CP-91-3003, pp. 75-82.

2. "Theoretical Research Investigation of High Energy Chemical Species", AF Contract Review, Edwards Air Force Base, California, April 3, 1991.

3. "Electronic Structure and IR Spectra of Dinitramide Salts", H. H. Michels and J. A. Montgomery, Jr., 1991 American Chemical Society Meeting, Atlanta, Georgia, April 14 -19, 1991.

4. "Electronic Structure, Thermochemical Properties and Propellant Performance Comparisons of Nitramines and Dinitramide Salts", H. H. Michels, J. A. Montgomery, Jr., and R. H. Hobbs, Air Force Contract Review, Edwards Air Force Base, California, June 1991.

5. "Electronic Structure, Thermochemical Properties and Propellant Performance Comparisons of Nitramines and Dinitramide Salts", H. H. Michels, J. A. Montgomery, Jr., and R. H. Hobbs, presented at SRI, International, Menlo Park, California, June, 1991.

6. "Electronic Structure, Thermochemical Properties and Propellant Performance Comparisons of Nitramines and Dinitramide Salts", presented at Wayne State University, Detroit, Michigan, October 21, 1991.

7. "Electronic Structure and Chemical Properties of Dinitramides - A New Class of Inorganic Oxidizers, H. H. Michels and J. A. Montgomery, Jr., 1992 Sanibel Symposia, St. Augustine, Florida, March 14 - 21, 1992.

8. "Electronic Structure and Thermochemical Properties of Dinitramide Compounds and Related Oxidizers" 6th Air Force HEDM Contractors' Meeting, Lancaster, California, April 12 - 15, 1992, pp. 48-55.

9. "Computational Studies of the Structure and Properties of Advance Propellants", H. H. Michels, J. A. Montgomery, Jr. And R. H. Hobbs, CSD review, San Jose , California, April 30, 1992.

10. "Studies of Chlorine- Free Properties: Thermophysical Properties, Composite Development, Synthesis Routes", H. H. Michels, AF Contract Review, Edwards Air Force Base, California, May 10, 1992.

11. "Electronic Structure and Thermochemical Properties of Dinitramide Compounds - A New Class of Inorganic Oxidizers", H. H. Michels and J. A. Montgomery, Jr., presented at the University of Georgia, December 3, 1992.

12. "Electronic Structure and Thermochemical Properties of Dinitramide Compounds - A New Class of Inorganic Oxidizers", H. H. Michels and J. A. Montgomery, Jr., presented at the University of Utah, January 11, 1993.

13. "Electronic Structure and Thermochemical Properties of Dinitramide Compounds - A New Class of Inorganic Oxidizers", H. H. Michels and J. A. Montgomery, Jr., presented at the University of Arizona, April 5, 1993.

14. "Chlorine-Free Energetic Oxidizers". H. H. Michels, J. A. Montgomery, Jr., and D. D. Tzeng, 7th Air Force HEDM Contractors' Meeting, Woods Hole, Massachusetts, June 6 - 8, 1993, PL-TR-93-3041, pp. 268-278.

15. "Structure, Thermochemistry and Performance of Advanced Propellants", H. H. Michels, J. A. Montgomery, Jr., D. D. Tzeng and E. Lee, 8th Air Force HEDM Contractors' Meeting, Crystal Bay, Nevada, June 5 - 7, 1994, PL-TR-94-3036, pp. 154-171.

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APPENDIX B-1

INVESTIGATION OF TWO POTENTIAL VISIBLE WAVELENGTH CHEMICAL LASER SCHEMES BASED ON THERMAL DISSOCIATION OF CHLORINE AZIDE

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ABSTRACT

Chlorine azide and fluorine azide were synthesized by the continuous titration of dilute HN_3 with dilute ClF and F_2, respectively. The reaction products were analyzed by both infrared and ultraviolet absorption measurements before a CO_2 TEA laser was used to pulse heat these energetic molecules in the presence of SF_6 (sensitizer) and either I_2 or CF_3I/XeF_2 gas mixtures. The resulting thermal dissociation of the energetic azides produced metastable halogen nitrenes which reacted by energy transfer to pump either the NF(b) or IF(B) states, which are potentially capable of lasing at visible wavelength. Time resolved emission spectroscopy was employed to follow these emitters as well as the metastable intermediates and I*, while the concentrations of the ground state dihalides were tracked by laser induced fluorescence. These data revealed that the global rate of I* quenching was negligible, the rate of NF(b) quenching by NF(a, X) was less than 6×10^{-12} cm^3/s, the yield of NCl(a) per ClN_3 molecule was 12% and the radiative rate of the NCl(a-X) transition was measured as 0.9/s in good agreement with a recent theoretical estimate by Yarkony. The yield of NCl(a) is explained by *ab initio* calculations of the ClN_3 potential surfaces which demonstrate that a singlet-triplet crossing occurs inside the barrier to dissociation. Large transient concentrations of IF(X), generated (in situ) by the thermally initiated reaction of XeF_2 with CF_3I, were also measured absolutely by a titration technique and (using this data) the effective rate of pumping of the interhalogen to its B state (by NF(a)/NCl(a) mixtures) was measured as 6.5×10^{-13} cm^3/s. This low rate is explained by NF(a) pumping out of vibrationally excited levels of the IF(X) state and NCl(a) pumping into vibrationally excited levels of the IF(B) state that lie above the predissociation limit. Thermal dissociation of the stable levels of the IF(B) state is also likely to occur at rates that are competitive with the spontaneous radiation. Additional work, focused on excitation of the NS(B-X) transition by chemical reactions of NF(a), is in progress.

THEORETICAL STUDIES OF SPIN-FORBIDDEN RADIATIONLESS DECAY IN POLYATOMIC SYSTEMS. II. RADIATIONLESS DECAY OF a-N_2O_2.

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ABSTRACT

The stability with respect to spin-forbidden radiationless decay of the previously reported [J. Chem. Phys. $\underline{88}$, 7248 (1988)] asymmetric dimer of NO, N-N-O-O (a-N_2O_2) is considered. The spin-allowed decay channel a-N_2O_2 ($^1A'$) $\rightarrow N_2O(X^1\Sigma^+)$ + O(^1D) is endoergic. However, the spin-forbidden decay channel a-N_2O_2($^1A'$) $\rightarrow N_2O(X^1\Sigma^+)$ + O(^3P) is exoergic. Large scale multireference configuration interaction wave functions, approximately 300,000 - 1,400,000 configuration state functions, based on double zeta polarization and triplet zeta polarization bases are used to study this process. The minimum energy crossing of the ground singlet $^1A'$ state and the lowest excited triplet $^3A''$ state was determined as was the interstate spin-orbit coupling. This electronic structure data was used in the context of a simple one-dimensional model to show that a-N_2O_2 is rapidly predissociated to $N_2O(X^1\Sigma^+)$ and O(^3P).

ON THE STRUCTURE AND THERMOCHEMISTRY OF HYDROGEN DINITRAMIDE

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ABSTRACT

Five stable conformations of hydrogen dinitramide have been identified through *ab initio* electronic structure calculations. The most stable has a secondary amine structure, $HN(NO_2)_2$, and a calculated heat of formation (0 K) of 28.4 kcal/mol. Four stable inorganic acid structures are found to lie 7.9 - 9.7 kcal/mol higher in energy. The predicted enthalpy of deprotonization of $N(NO_2)(NOOH)$ is $\Delta H_{acid}(298 \text{ K}) = 302.6 \pm 2$ kcal/mol, making this one of the strongest known gas-phase inorganic acids. We estimate the electron affinity of the $N(NO_2)_2$ radical to be 5.0 ± 0.5 eV and the N-N bond dissociation energy of $HN(NO_2)_2$ to be 48 ± 8 kcal/mol. It is shown that unimolecular decomposition is the most likely low-energy decomposition mechanism for hydrogen dinitramide.

STRUCTURE AND STABILITY OF TRINITRAMIDE

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ABSTRACT

Ab initio calculations of the structure and thermochemistry of trinitramide, $N(NO_2)_3$, are reported. A vibrationally stable C_3 structure having 1.545 Å N-N bond lengths is found at the MP2/6-31G* level of theory. The heat of formation of trinitramide is estimated to be 59 kcal/mol. Thermal decomposition of trinitramide most likely occurs via N-N bond cleavage, which is estimated to require 26 kcal/mol.

APPENDIX B-5

ENERGY TRANSFER FROM METASTABLE NF TO BORON HYDRIDE

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ABSTRACT

Gas phase reaction of B_2H_6 with HN_3 at 400°C yields tetraazidodiborane (TADB), which subsequently dissociates into two diazidoborane molecules. Exposure of TADB to vibrationally excited SF_6 generates free BH radicals that may be pumped by energy transfer from metastable $NF(a^1\Delta)$ molecules, obtained by simultaneous dissociation of FN_3. Even though BH radicals are rapidly consumed, the transient yields approach 2% of initial donor concentration. The rate constants for sequential excitation of the $a^3\Pi$ and $A^1\Pi$ states of BH by $NF(a^1\Delta)$ are estimated to be ~8 x 10^{-10} and ~3 x 10^{-11} cm^3/s, respectively, and transient population inversions with peak optical gains of 10%/cm are developed on the BH(A-X) transition at 433 nm.

STRUCTURES, BONDING, AND ENERGETICS OF N_2O_2 ISOMERS

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ABSTRACT

The structures and energetics of the N_2O_2 isomers are predicted at several levels of theory. Both single reference and multireference based correlated methods were used to determine the structures and relative energies. Five high-energy minima were located above 2NO with QCISD(T)/6-311+G(2df)//MP2/6-311+G(d) (PT2F/6-311+G(2df)//MCSCF/6-31G(d)) relative energies of ca. 38 (51), 46 (51), 61 (74), 69(74) and 68 (80) kcal/mol for 1,2-diaza-3,4-dioxacyclobutene (1), bond stretch 1,3-diaza-2,4-dioxa[1.1.0]bicyclobutane (2), a-N_2O_2 (3), 4, and 1,3-diaza-2,4-dioxa[1.1.0]bicyclobutane (5), respectively. The effect of basis sets on structures is small within a given level of theory. The MCSCF structures agree reasonably with those of MP2.

THEORETICAL PREDICTION OF THE STRUCTURES AND STABILITIES OF AZIDAMINES

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ABSTRACT

Ab initio molecular orbital and density functional theory calculations show that azidamines, a new family of polynitrogen compounds, are minima on their respective potential energy surfaces. The geometries, vibrational frequencies, and heats of formation are predicted for $N(N_3)_3$, $HN(N_3)_2$, the $N(N_3)_2^-$ anion, and the $N(N_3)_4^+$ cation. All of these compounds are highly energetic materials with large positive heats of formation. The results suggest that these polynitrogen compounds could be synthetically accessible, and potential methods for their syntheses are proposed.

HIGH SPECIFIC ENTHALPIES FROM THE PHOTOCHEMICALLY INDUCED ISOMERIZATION: BOH ↔HBO

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ABSTRACT

The photochemical interconversion of BOH to the considerably more stable HBO isomer is evaluated. The BOH and HBO isomers, while differing considerably in energy, possess a significant barrier to interconversion on the ground $^1A'$ potential energy surface. However, by accessing the low-lying double minimum a $^3A'$ state, we define an interconversion pathway that facilitates the interconversion process, allowing a substantial energy release. Here, we calculate the potential surfaces for the X $^1A'$ and a $^3A'$ states of HBO ↔ BOH and present limited evaluations for the b $^3A''$ and A $^1A'$ states. We outline means to distinguish the BOH and HBO isomers, following the progress of the isomerization process using optical, infrared, and mass spectrometric techniques. The energetics of this geometric isomerization process and the potential utilization of BOH as a storable high energy material are discussed.